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Liquid Structure and Energy of Vaporization

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The equation derived by Hildebrand and Wood for the potential energy of a liquid in terms of its structure, as determined by x-ray scattering, has been tested by the aid of the structures determined by Thomas and Gingrich for potassium at 70° and 395°. The ratio of the energy of vaporization is calculated to be 1.154 while the same ratio as determined by aid of the vapor pressure curve is 1.155. The decrease in the van der Waals a is the same for potassium and benzene for temperature intervals corresponding to equal expansion ratios.

HILDEBRAND and Wood,[1] in 1933, derived the equation

$$E' = \frac{2\pi N^2}{v} \int \epsilon W r^2 dr \qquad (1)$$

connectng the potential, ϵ, of the London forces between two molecules with the potential energy, E', of a mole of these molecules in the liquid state. Here N is the Avogadro number, v the molal volume of the liquid and W is the so-called distribution or probability function which expresses the structure of the liquid. If we consider a spherical shell of thickness dr at a distance r from a given central molecule, the number of molecular centers in this shell when r is large is its volume times the density of molecular centers, but when r is small the variable W is required.

The studies of London[2] indicate that ϵ obeys an inverse sixth-power law so far as attraction is concerned. Repulsion is much steeper and can be neglected with little error, hence, writing $\epsilon = -k/r^6$, the above equation becomes

$$E' = \frac{-2\pi N^2 k}{v} \int \frac{W}{r^4} dr. \qquad (2)$$

An interesting application of this equation is made possible by the recent determinations of W over a wide range of temperature for sodium and potassium by x-ray studies by Gingrich[3] and coworkers. The variation of W with temperature agrees, in type, with the prediction made by myself[4] and with the behavior of an artificial model worked out by Morrell.[5] Professor Gingrich has kindly furnished me with his original curves for potassium at 70° and 395° from which I have plotted[6] W/r^4 against r. A graphic integration of the area under each curve showed them to be in the ratio 0.95, the curve for the higher temperature, of course, being the smaller, because of the

[1] (a) J. H. Hildebrand and S. E. Wood, J. Chem. Phys. **1**, 817 (1933); (b) J. H. Hildebrand, *Solubility* (Reinhold Publishing Corporation, 1936), pp. 66–68.
[2] F. London, Zeits. f. Physik **60**, 491 (1930); Zeits. f. physik. Chemie, **B11**, 222 (1930).
[3] F. H. Trimble and N. S. Gingrich, Phys. Rev. **53**, 278 (1938); C. D. Thomas and N. S. Gingrich, J. Chem. Phys. **6**, 411 (1938).
[4] Reference 1(b), p. 97.
[5] W. E. Morrell and J. H. Hildebrand, J. Chem. Phys. **4**, 224 (1936).
[6] Cf. reference 1(b), p. 71.

less defined structure. We may assume that the energies of vaporization of the liquid, at the two temperatures, ΔE_{343} and ΔE_{768}, bear the same ratio as the potential energies at the same temperatures, hence $\Delta E_{343}/\Delta E_{768}=v_{768}/0.95v_{343}$. The molal volumes have been calculated from the equation for the density, $d^t=0.826-0.0222(t-62.5)$, given by Rinck,[7] yielding 52.0 cc at 395° and 47.4 cc at 70°. These values give $\Delta E_{343}/\Delta E_{768}=1.154$.

To check this calculation I have used the equation for the heat of vaporization of liquid potassium, $\Delta H=21{,}788-2.73T$, given by Kelley[8] in his excellent critical summary of data pertaining to the metals. This corresponds to $\Delta E=21{,}788-4.72T$, whence $\Delta E_{343}/\Delta E_{768}=1.155$. The extremely close agreement with the value above is doubtless fortuitous, for no such accuracy can be claimed.

In view of the frequent use of the equations, $(\partial E/\partial v)_t=a/v^2$ and $\Delta E=-a/v$, it is interesting to note that the factor 0.95 for the ratio of the integrals of $(W/r^4)dr$ for potassium for these two temperatures gives an idea of the extent to which the "constant" a falls off with temperature. I have examined experimental evidence of this in an earlier paper[9] from which the figures for benzene may be quoted.

t	0	20	40	60	72.5	80
v, cc	86.65	88.8	91.0	93.4	95.0	96.0
$a=v\Delta E$ (atmos. $\times$ cc$^2\times 10^{-4}$)	2790.	2750.	2715.	2675.	2650.	2630.

Let us assume that the decrease in the value of the integral of $(W/r^4)dr$ is determined only by the expansion of the liquid on increasing the temperature. The liquid potassium at 395° has a volume $52.0/47.4=1.096$ times its volume at 70°. Benzene is equally expanded over its volume at 0° when its volume is 1.096×86.65 or 95.0 cc. This volume is reached at 72.5°. The value of a at this temperature is 2650×10^4, which is 0.95 of its value at 0°, exactly the same decrease as for potassium through the corresponding interval. The validity of the inverse sixth-power variation for attractive potential is, of course, something of an assumption in the case of metals so that the apparent applicability of Eq. (2) to potassium must be regarded as suggestive rather than conclusive.

[7] E. Rinck, Ann. chim., **18**, 395 (1932).
[8] K. K. Kelly, Bull. No. 383, U. S. Bur. Mines.
[9] J. H. Hildebrand, Phys. Rev. **34**, 984 (1929).

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Scattering of Slow Electrons in, and Apparent Electron Affinity of Boron Fluoride

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Slow electron scattering in boron fluoride exhibits a phenomenon similar to that observed in mercury. An inverse fourth-power attraction law is indicated and the apparent electron affinity may be roughly estimated. A possible correlation between electron affinity and bands observed in the spectra is postulated.

A RELATION between the scattering of slow electrons by a molecule and its electron affinity has recently been proposed by the authors[1] and shown to be in agreement with the experimental results in the case of mercury vapor. The scattering of slow electrons in boron fluoride has now been measured; and while the experiments are not accurate enough to be conclusive, they are consistent with the previously proposed relationship.

Boron fluoride was chosen since its chemical properties indicate a strong tendency to hold on to electrons and it may be readily handled in a glass system. The tube in which the electron beam was produced and the scattering measured

[1] Simons and Seward, J. Chem. Phys. **6**, 790 (1938).

was the same as used in the mercury vapor experiments. The pressure of the gas was measured by a McLeod gauge. Measurements were taken with electrons of varying voltages at a series of pressures ranging from 5×10^{-4} mm to 30×10^{-4} mm. Operation of the hot tungsten filament caused a continual increase in the pressure in the tube; and although it was frequently determined, errors of ±10 percent in the recorded pressures for this reason are possible. Presumably for this reason the values of α, the apparent cross section effective in scattering, calculated from the different pressures are not as consistent as was hoped. This pressure increase is probably caused by the release of adsorbed material from the glass and metal of the tube, as the pressure slowly decreased when the filament current was stopped. It is unlikely that a chemical reaction or decomposition of the boron trifluoride caused it, as any probable one would result in a decrease rather than an increase in pressure.

With measurements at five different pressures, values of α were calculated at each voltage from all possible pairs of pressures by means of the equation $\alpha=(2.3/l(p_2-p_1))\log R_1/R_2$, in which l is the length of the scattering chamber, p_1 and p_2 the pressures, and R_1 and R_2 the ratios of unscattered current to total current at the pressures p_1 and p_2, respectively. The average of the values thus obtained are tabulated in Table I with the mean deviation from each average.

It may be seen that like mercury the values of α are rising at the lowest voltage employed. Values of $\alpha V^{\frac{1}{4}}$, corresponding to inverse fourth-power attraction are likewise constant within the limits of accuracy of the experiments up to the minimum in the curve at six volts.

TABLE I.

VOLTAGE	α	MEAN DEVIATION	$\alpha V^{\frac{1}{4}}$
2	84.0	11.1	134
4	66.8	5.6	169
6	47.8	6.9	159
8	55.0	2.7	220
10	52.7	3.9	244
12	55.7	6.2	291
14	61.2	8.9	354

Calculation of the apparent electron affinity of boron fluoride by the method previously employed requires a knowledge of the distance of the added electron from the attracting center when a stable negative ion is formed. The apparent electron affinity as a function of radius is $(4.3\times10^{-24})/r^3$. If the covalent radius of boron, 0.89A, is used the calculated apparent electron affinity becomes 6.1 electron volts. This radius is probably too small since the electron in a negative ion would presumably be found at a greater distance from the center than the electrons in a neutral molecule.

In the spectrum of boron fluoride[2] there are four diffuse bands in the visible region. No explanation of the origin of these bands seems available. It may be that light producing these bands is emitted when the boron fluoride molecules capture electrons to form negative ions. If this suggestion be correct, it would explain the existence of four bands. To complete its octet the boron atom requires two electrons. Although the second of these would be added to a particle with a negative charge, the addition of the eighth electron to complete an octet would be expected to involve greater energy than the addition of the seventh; and this may partially compensate for the charge repulsion. Two bands not greatly different in frequency may thus be produced. The existence of two isotopes of boron in appreciable quantities would double this number to four.

The spectrum lines referred to are in the region of $\lambda=5800$, corresponding to about two electron volts. Should we assume an ion radius of 1.3A, a not unreasonable value, the calculated apparent electron affinity would become two electron volts, indicating a possible correlation between the scattering experiments and the spectral studies. If this correlation should be proven correct, further study of the spectra of this or a similar compound may enable the quantum conditions to be evaluated and a precise value of the electron affinity calculated.

[2] Dull, Phys. Rev. **47**, 458 (1935).

The Blackening of Zinc Sulfide Phosphors

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The process of blackening of zinc and cadmium sulfide phosphors is studied experimentally and theoretically. A survey of the principal experimental facts is given and several new experiments are described. It is suggested that the blackening of the sulfide salts is a two-quantum process in which both positive and negative charges are released from the interior; these charges move to the surface and there produce electrolysis in a film of moisture that is present on the surface when the specimen is in damp air. This picture will explain the known experimental facts concerning the blackening process. The important differences between the blackening of sulfides and the print-out effect in photographic emulsions are discussed.

I. INTRODUCTION

THE blackening of alkaline earth sulfides under exposure to ultraviolet light has been studied by many investigators,[1] and several important conclusions have been established. We shall survey these conclusions in the present paper, and shall augment them with the results of a number of experiments that have been carried on in this laboratory. In addition, we shall present a detailed atomic picture which appears to correlate the experimental facts.

Although there are striking differences between the details of the facts concerning the blackening of the sulfides and the blackening of silver halides, there is a close correspondence between the interpretation which we shall present for the sulfides and that which Gurney and Mott[2] have presented for the print-out effect in photographic emulsions.

II. EXPERIMENTAL OBSERVATIONS

We shall classify the principal experimental conclusions concerning the blackening of sulfides into six divisions.

A. Correlation with luminescence

Only sulfides which are luminescent darken appreciably under ultraviolet light.[3] This law has been established only for zinc and cadmium sulfides, the substances with which practically all darkening experiments have been carried out. These sulfides may be formed by an aqueous precipitation method, and it is found that they may be darkened only after they have been subjected to a thermal treatment which is identical with that which is necessary to transform them into phosphors. In the simplest cases, this procedure consists in heating the pure material at 950°C for about an hour or at lower temperatures for a longer time.[4] The change which accompanies heating has been interpreted to be the introduction of neutral zinc or cadmium atoms into the interstices of the zinc or cadmium sulfide lattice.[5] Zinc or cadmium sulfides which have been activated with copper or silver and which presumably contain interstitial copper or silver atoms also darken.

Another test of the hypothesis that only the phosphorescent materials darken is provided by the following experiment. The luminescent properties of zinc or cadmium phosphors may be destroyed by placing them under high non-hydrostatic pressure, such as may be obtained

[1] W. J. O'Brien, J. Phys. Chem. **19**, 113 (1915); P. Lenard, *Handbuch der Experimental Physik*, Vol. 23, 1 and 2; Eibner, Chem. Zeits. **B4**, 474 (1920); Chem. Zeits. **47**, 13 (1923). E. Maass and R. Kempf, Zeits. Ange. Chem. **35**, 609 (1922); **36**, 293 (1923). A. Schleede, Zeits. f. physik. Chemie **106**, 386 (1923). A. Job and G. Emschwiller, Comptes rendus **177**, 313 (1923). We are indebted to Professor K. Fajans for a copy of an unpublished thesis of E. Becker which contains an excellent summary of the experimental material prior to 1927 and a large amount of new material on the darkening process. Some of his results are described in the text.

[2] R. W. Gurney and N. F. Mott, Proc. Roy. Soc. **164**, 151 (1938). See also the paper of J. H. Webb and C. H. Evans (J. Opt. Soc. Am. **28**, 249 (1938)) for a discussion of new experimental work which supports this theory.

[3] Becker (reference 1) reports that unheated sulfides, which presumably are not luminescent, may be darkened slightly by long exposure to ultraviolet light. We have not been able to obtain appreciable darkening in times as short as Becker has.

[4] E. Teide and E. Weib (Ber. **65**, 371 (1932)) report that zinc sulfide may be activated with copper at 330° by "long" heating.

[5] F. Seitz, J. Chem. Phys. **6**, 454 (1938).

in an ordinary hydraulic press. According to the interpretation advanced by one of us, the phosphors are thermodynamically unstable at room temperature, and thermodynamical equilibrium, in which the interstitial atoms are precipitated out, is obtained by means of pressure. It is found that the phosphors do not darken appreciably after they have been pressed enough to destroy their luminescence.

B. The effect of moisture

The great dependence of darkening upon the presence of moisture has been observed and pointed out by many investigators. It is found that a specimen of zinc sulfide which is in damp air will darken thousands of times more rapidly than a specimen which is placed in a desiccator under identical conditions of illumination. For example, a specimen of zinc cadmium sulfide activated by copper which was placed in an evacuated quartz tube did not darken in 2000 hours of exposure at a distance of six inches from a low pressure mercury lamp.[6] An identical specimen placed in air saturated with moisture becomes very dark in one-half hour.

C. Spectral sensitivity

The spectral sensitivity curve for darkening was investigated roughly by Lenard, Job and Emschwiller, and by Becker. These workers exposed zinc sulfide to radiation from mercury lamps and found maximum blackening in the neighborhood of 3129A. We have investigated this problem further and believe that these workers obtained maximum darkening in the neighborhood of 3129A only because they used mercury lamps in which the 3129 line was more intense than lines of shorter wave-length. On investigating the darkening effect of the 3650, 3341, 3128, 2804, 2752 and 2536 lines of mercury at equal intensity, we observed that maximum darkening occurs near the 2752 line. The darkened specimens were mounted on glass slides and were placed in a humidor with a quartz window through which the radiation was focused on the specimen.[7] The phosphorescent powders were fastened with a small amount of collodion binder. It is possible that this cut the intensity of the short wave-length lines slightly, so that the peak for blackening may be lower than 2752. The 3650 line had the weakest effect of all. It produced appreciable blackening only after very long exposures at high intensity. The peak of the spectral sensitivity curve for luminescence in zinc sulfide is in the vicinity of 3650A, showing that the production of blackening requires harder quanta than the production of luminescence.

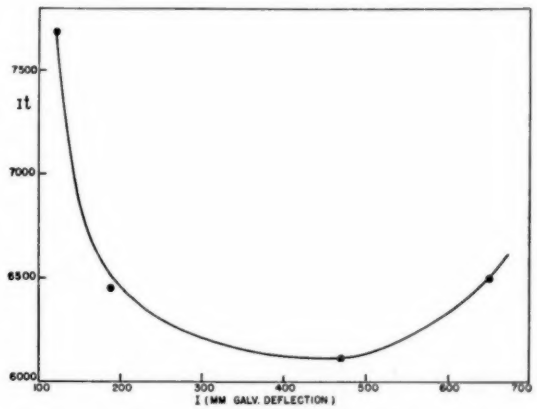

FIG. 1. I_t *versus* I curve for constant blackening of zinc sulfide phosphor. The unit of intensity is one millimeter of deflection of the thermopile galvanometer. This system has a sensitivity of 0.75 microwatt per mm. The unit of time is one minute. The standard of blackening of this curve is a ten-minute exposure at 650-mm deflection.

Figure 1 shows an exposure *versus* intensity curve for the production of blackening by the 3129 line. The standard of darkening for this curve was taken to be that produced by a ten-minute exposure at full line intensity which was 650-mm deflection on the thermopile galvanometer.[8] This is the 6500 point on the I_t scale of the figure. The same blackening was then duplicated at lower intensities. It should be noted that the curve rises at both low and high intensities, just as the corresponding curves for photographic emulsions do,[9] showing that there is an optimum intensity for efficient blackening. The intensities of the other available lines that produce blackening were so low that all of their I_t *versus* I curves correspond to the steep portion of the left-hand side of Fig. 1.

[6] This quartz lamp, operating at 50 v and 0.5 amp. produces about 16 percent of its radiant energy at 2536Å.

[7] We are indebted to Mr. Frank Benford of this laboratory for the use of the powerful quartz monochromator with which this work was done.

[8] The sensitivity of this system is 0.75 microwatt per mm. The slits were 1 mm wide.

[9] J. H. Webb, J. Opt. Soc. Am. **23**, 157 (1933).

FIG. 2. The manner in which the discrete levels of the centers allow the electron and hole to separate by a two step procedure. A quantum of frequency ν_1 raises the electron from the discrete level to the conduction band giving rise to a free electron. A quantum ν_2 subsequently raises an electron from the filled band to the level of the center, giving a normal center and a free hole.

D. Decomposition products

Job and Emschwiller[1] found by a chemical investigation that the principal substances produced during the process of blackening of zinc sulfide are free zinc and sulfur. In addition, they found traces of H_2S, SO_2 and of hydrosulphonic acids, which may be explained as decomposition products of the sulfur in the presence of water. There seems to be no limit to the extent to which blackening may proceed under appropriate conditions. Job and Emschwiller continued illumination until ten percent of the zinc sulfide was decomposed.

E. Additional factors which influence the rate of blackening

The rate at which blackening proceeds may be influenced by factors other than humidity. It is common experience that traces of sodium chloride that are left in the phosphor speed up blackening. Becker[1] has shown that other good electrolytes behave in a similar manner. He studied the blackening of zinc sulfide suspended in four normal solutions of zinc and barium salts, and found that the rate was about ten times faster in these than in pure water.

F. Reversal

Slightly darkened samples of zinc sulfide become white again if they are left in the dark, showing that there is a spontaneous reversal of darkening. This reversal is dependent upon humidity and will not occur if the specimen is placed in a desiccator. In addition, the reversal may be speeded up by a large factor by moistening the darkened material with a concentrated sodium chloride solution.

III. INTERPRETATION

The production of luminescence in the sulfide phosphors is accompanied by photoconductivity, indicating that electrons are liberated from the centers. We shall conclude from the correlation between luminescence and darkening that these free electrons are essential for darkening. The fact that the spectral sensitivity curve for darkening is not the same as that for photoconductivity shows that radiation is essential for a process other than the production of free electrons. We shall postulate that the freed electron either recombines with an ionized center producing phosphorescent light, or becomes trapped at the surface. If the crystal were in a vacuum, the trapped electron eventually would be released thermally and would return to the interior of the crystal, where it could recombine with an ionized center. If the crystal surface were moist, however, the negative charge of the trapped electron should attract a cloud of positive ions which should make the surface state more stable. The positive ions probably are the zinc ions of dissolved zinc sulfide in the case of pure water. The concentration of ions will be larger if the water contains a high concentration of a good electrolyte.

If the positive charges that are attached to the ionized centers were not released, the surface of the crystal would become negatively charged relative to the interior, and the electrons eventually would stop going there. Apparently, the spectral sensitivity curve for blackening is characteristic of the absorption process in which an electron is transferred from a sulfur ion of the crystal to the ionized center, producing a neutral center and a free hole in the band of sulfur electronic levels (cf. Fig. 2). The fact that the band for blackening is broad is in qualitative agreement with this. The energy required to obtain photoconductivity in pure zinc sulfide should be about the same as the sum of the energies of the peaks of the optical sensitivity curves for photoconductivity and for blackening of the phosphor. It is not safe to say that the threshold for the one quantum process is less than the sum, because, as Mott[10] has pointed out, thermal excitation may play an appreciable role

[10] N. F. Mott, Proc. Roy. Soc. **167**, 384 (1938).

in the production of free electrons and free holes; that is, the peaks for photoconductivity may correspond to transitions to discrete levels which lie beneath the ionization limits, and thermal fluctuations may provide the additional energy that is necessary to complete the ionization process. The energy of the peak for photoconductivity in the phosphor is about 3.5 ev and that for blackening is about 4.5 ev, so that the sum is about 8 ev. Thus, photoconductivity should appear in pure zinc sulfide near 1500A if our interpretation of the darkening spectral curve is correct. This wave-length actually lies in the fundamental absorption region of the crystal. The absorption is already strong at 2536A.

When the free positively charged holes reach the surface, they should act like singly charged sulfur ions and should attract negative ions from solution. The formation of free zinc and free sulfur may be looked upon as the electrolysis of zinc sulfide by the e.m.f. which has its origin in the separated Zn^+ and S^- ions. It would be exceedingly speculative to propose a detailed mechanism for this process. A plausible supposition is that the positive and negative charges become attached to ions of the solution, forming free Zn^+ and S^- ions which combine to form free zinc and sulfur according to the reactions

$$2Zn^+ \rightarrow Zn^{++} + Zn,$$
$$2S^- \rightarrow S^{--} + S.$$

The reaction

$$2Zn^+ + S^- \rightarrow Zn^{++} + S^-$$

should also occur, of course, and should decrease the total efficiency of production of zinc and sulfur.

According to this picture, the interior of the zinc sulfide crystal should be left unaltered in the final state, since the centers are not depleted during the blackening. They play much the same role as a catalyst in an ordinary reaction. Since the ratio of centers to ordinary atoms may be as low as 10^{-4}, it is necessary that the centers play this kind of role if as much as ten percent of the bulk material may be decomposed.

The spontaneous reversal of blackening in the presence of conducting water indicates that the reaction

$$Zn + S \rightarrow ZnS$$

takes place electrolytically. This should be speeded up by increasing the electrolytic conductivity of the solution.

The decrease of efficiency of blackening at low intensities, as indicated by Fig. 1, probably occurs because of the spontaneous reversal of blackening, since the forward and backward rates should be equal for sufficiently low intensity. The high intensity decrease may have many explanations. For example, the trapped electrons may be released by light, or the spontaneous reversal of darkening may be speeded up at high intensities.

IV. Conclusion

The blackening of zinc sulfide phosphors is analogous to the print-out effect of silver halide emulsions. There are, however, several major differences between the two processes. The print-out effect seems to be a one-quantum effect; the darkening of phosphors is a two-quantum process. The positive charge which is left behind by the released electrons seems to be removed by ionic conduction in the silver salts and by a secondary photoconducting process which requires short wave-length light in the sulfides. The photolysis occurs within the crystal granules in photographic emulsions; it occurs electrolytically in an adsorbed film of moisture on the sulfide crystals. In a similar way the spontaneous reversal of blackening seems to be an aqueous electrolytic effect in the sulfides but not in the silver salts.

A Further Study of the Absorption of Aqueous Solutions at 4.72μ

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(Received October 6, 1938)

By the use of a grating spectrometer, the infra-red absorption spectra of aqueous solutions of five inorganic materials (KI, $CuBr_2$, $ZnBr_2$, $CdCl_2 \cdot 2H_2O$, and NaOH) and six organic materials (acetone, CH_3COONa, CH_3COONH_4, cane sugar, C_6H_5OH, and C_2H_5OH) were observed in the region of the water band at 4.72μ. The organic materials investigated caused a displacement of the position of maximum absorption to shorter wave-lengths; the inorganic materials apparently caused a shift to longer wave-lengths, but the actual effect on the water band may be masked by other absorption bands in the same region. The concentration-shift relationship was investigated for some of the materials. Size of the solute molecule and the positive ion seemed to be of comparatively little importance.

IN a previous paper[1] on which one of us collaborated, a report was made on an investigation of the effect of dissolved halogen salts on the 4.72μ water band, using a prism spectrometer. This band is well suited for a study of the effects due to solutes since it arises from association of the water molecules. It was desired to supplement this work with additional investigations of the infra-red spectra of more complex inorganic materials and of certain typical organic materials.

In order to work with more favorable dispersion, in case other bands should be found in the immediate vicinity of the 4.72μ band, the present work was done on the grating spectrometer built under the direction of Dr. E. K. Plyler at the University of North Carolina.[2] This spectrometer is of the usual type, employing a fore prism of rocksalt to separate the orders, and supplied with a five-inch echelette grating, ruled 4800 lines to the inch. The effective slit width used was approximately 2 cm^{-1}. The wave-length of the radiation falling on the thermocouple for any setting of the grating could be calculated from the circle reading by using the reflection grating formula, $n\lambda = K \sin\theta$, where n is unity and K has the value 10.566μ. The central image corresponded to a circle reading of 81° 20′. Observations were taken at intervals varying from approximately 0.01μ to 0.05μ. The absorption cells were prepared as in the previous study.

In Fig. 1 are shown transmission curves for water (A), and solutions of potassium iodide (B) and acetone (C, D). The curve for water is included at the top of each figure for comparison, and a line is drawn through the point of maximum absorption so that the displacements of the band of the solutions may be noted readily. In order to determine whether the band observed previously for the potassium iodide solution with the prism instrument was single or composed of two or more neighboring bands, readings were taken at intervals of approximately 0.01μ. Curve 1 B was obtained in this manner and gives no indication of secondary structure. This indicates that the observed displacement is not caused by the presence of a side band, but by a shifting of the water band as a whole. The position of maximum absorption for this 4 M solution occurs at 4.90μ (erroneously given as 5.85μ in the reference cited). Curves 1 C and 1 D show the variation in the amount of displacement with concentration in the case of acetone. It is seen that both the 25 percent solution and the 50 percent solution cause a displacement of the band toward shorter wave-lengths, the more concentrated solution producing the greater shift. Because of the broadness of the band, no attempt has been made at this time to make a quantitative study of the relationship between concentration and amount of displacement. It is also seen from Fig. 1 that the introduction of different solutes may cause a displacement of the water band toward either longer or shorter wave-lengths.

Transmission curves for solutions of two acetic

* Now at Tulane University.
† Now at Furman University.
[1] Plyler and Barr, J. Chem. Phys. 6, 316 (1938).
[2] Shearin and Plyler, J. Opt. Soc. Am. 28, 61 (1938).

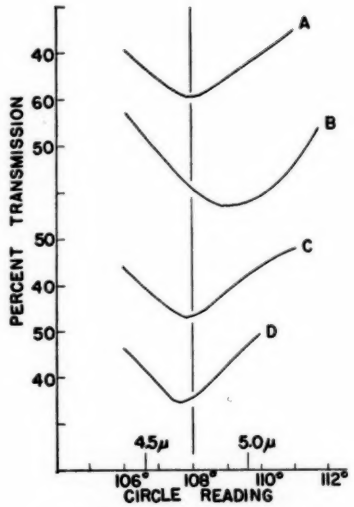

FIG. 1. The transmission of water (A) and aqueous solutions of (B) 4 *M* KI, (C) 25 percent by volume acetone, and (D) 50 percent by volume acetone.

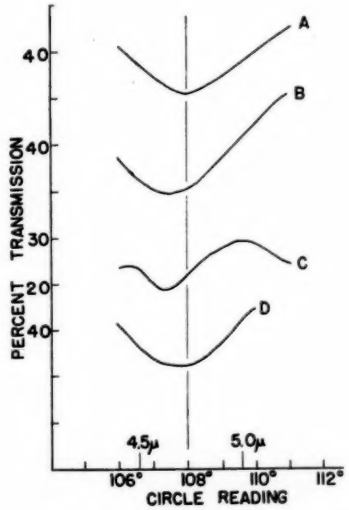

FIG. 2. The transmission of water (A) and aqueous solutions of (B) 3 *M* CH_3COONa, (C) 7 *M* CH_3COONH_4, and (D) 10 percent by weight cane sugar.

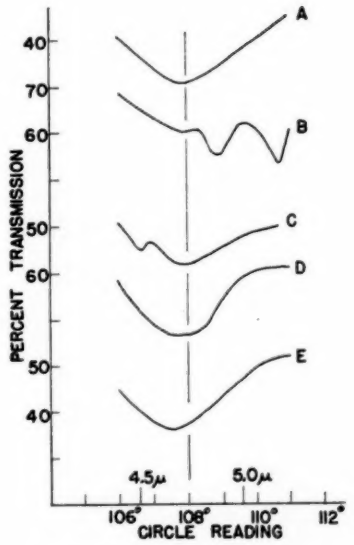

FIG. 3. The transmission of water (A) and aqueous solutions of (B) phenol, concentrated, (C) phenol, dilute, (D) 50 percent by volume C_2H_5OH, and (E) 25 percent by volume C_2H_5OH.

acid salts, sodium acetate (B) and ammonium acetate (C), are shown in Fig. 2. There is an apparent shift to shorter wave-lengths in the case of both of these salts, but this may be caused by the overlapping of other bands corresponding to materials formed through hydrolysis.[3] It is also possible that certain groups of atoms in these molecules could produce overlapping bands; for example, the ammonium group is known to absorb in the region of 4.5μ.

In order to determine whether the size of the solute molecules was an important factor in producing the shift, the spectrum of a 10 percent solution of cane sugar was obtained. This material was selected also because of its lack of ionization in solution. As is seen from Fig. 2 (D), this large molecule produces no marked change in the position of the water band; there is, however, some broadening of the band. This indicates that while the sugar molecules form no strong linkages with the water molecules, they serve to separate them to some extent.

As is well known, at room temperature aqueous solutions of phenol exist in two ranges of concentration, one dilute and the other quite concentrated. The two solutions used were prepared at room temperature by adding phenol to water until saturation for the dilute solution, and adding water to phenol for the concentrated solution. The estimated concentrations were 8 percent and 72 percent phenol, respectively. The absorption spectra of these solutions were obtained and the results are shown in Fig. 3 (B, C). Since in the concentrated solution there is a preponderance of phenol, the bands caused by the solute itself which are found in this region prevent the observation of any possible change in the position of the water band. There is a slight shift to shorter wave-length found for the dilute solution, and it is interesting to notice that a new band has appeared in the neighborhood of 4.5μ. This may be due to the linking of OH groups with water molecules, since this band is observed in all solutions containing OH ions.

The curves D and E in Fig. 3 show the observed transmission for 50 percent and 25 percent solutions of ethyl alcohol. A shift to shorter wave-lengths is seen for both solutions, the more dilute solution giving the greater shift of the water band. No band was observed in the region of 4.5μ, as in the case of the dilute phenol solution, but, since alcohol does not ionize

[3] Plyler and Gordy, J. Chem. Phys. 2, 470 (1934).

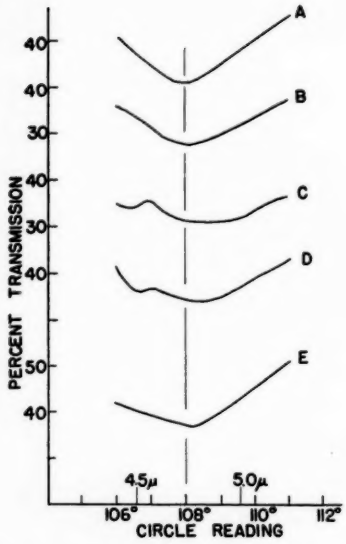

FIG. 4. The transmission of water (A) and aqueous solutions of (B) 1.25 *M* $CuBr_2$, (C) 4 *M* $ZnBr_2$, (D) 4 *M* $CdCl_2 \cdot 2H_2O$, and (E) 1 *M* NaOH.

appreciably in water, this difference was to be expected.

As the previous work on the halogen salts was confined to comparatively light, univalent positive ions, the spectra of three inorganic materials containing, respectively, copper, zinc and cadmium were observed and the results are shown in Fig. 4. In each case there is a shift of the water band to longer wave-lengths. The bands at about 4.5μ in curves C and D are attributed to hydrolysis products, since hydrated OH ions give rise to a band in this region. The investigation of solutions of halogen salts with heavy positive ions was not carried further because of the interference of these bands, and because of the impossibility of obtaining suitably concentrated solutions. For the comparatively dilute NaOH solution it is seen that the intense absorption of the hydroxide has distorted the water band on the short wave side. A slight shift to longer wave-lengths of the maximum absorption of water is seen, despite the presence of the distortion.

Solutions of 7 *M* $ZnCl_2$ and 5 *M* $Al_2(SO_4)_3 \cdot 18H_2O$ were also investigated, but any effect of the solute on the water band was masked by the strong general absorption throughout the region studied.

It seems quite probable that, in addition to the displacements commented upon above, the presence of the solutes may cause a change in the intensity of the water band, as has been observed in other cases.[4] This possibility was not examined in the present work, however, since the construction of equivalent water cells was not feasible, because of the fact that the absorption cells used were necessarily limited in thickness to about 0.02 mm because of the large coefficient of absorption of water in this region.

From an examination of the foregoing transmission curves it seems that there is no direct correlation between the observed shift in the position of the water band and (1) size of molecule of solute, (2) size of positive ion and (3) valency of positive ion. There has not been found any simple relationship as was found in the previous work on the simpler and lighter halogen salts. Because of the hydrolyzation which takes place in the case of the salts selected, with accompanying production of bands in the region of study, any regular shift due to size and valency of the positive ions may have been masked. However, if such an effect does exist, its magnitude is not comparable with that produced by the halogen ions, since otherwise the shifts could have been seen superimposed on the bands due to hydrolysis.

The change in the absorption of water at 4.72μ caused by organic solutes seems to be influenced more by the nature of the molecule than by its size. Thus we find that in the case of ethyl alcohol a 25 percent solution shows more shift than the 50 percent solution, while the acetone solutions showed the reverse effect.

In no instance where a shift was found did it seem to be caused by the formation of another band in addition to the 4.72μ band, and it is therefore concluded that the shift is always the result of a displacement of the band as a whole. These results indicate that a considerable change may be produced in the associational water band at 4.72μ by the presence of solutes, but from the information obtained so far it cannot be predicted which way the position of maximum absorption would be shifted for a given solute.

The writers wish to express their appreciation of the constructive criticism and helpful suggestions of Dr. E. K. Plyler of the University of North Carolina.

[4] Grantham, Phys. Rev. **18**, 339 (1921).

The Infra-Red Transmission of Several Organic Compounds Near the Melting Point

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The transmission of benzophenone, desoxybenzoin, diphenyl ketone, and benzalacetophenone has been measured at various temperatures. The spectra of the compounds are affected only slightly by change of state, the most marked difference being a variation in the intensity of certain bands. Isochromatic curves for benzophenone and desoxybenzoin indicate pronounced differences in background transmission at temperatures immediately below the melting point with a rapid increase at the melting point, while those for dibenzyl ketone and benzalacetophenone show only a rapid increase in transmission on melting. The data for benzophenone and desoxybenzoin are interpreted as indicating the existence of a mesophase near the melting point.

ERRERA[1] has reported dielectric losses in the anisotropic phase of liquid crystalline compounds; Ornstein and Kast[2] have reported a similar phenomenon in the case of benzophenone at temperatures near the melting point. An infra-red study of liquid crystals[3] has shown a modified background transmission in the mesophase (anisotropic). The present investigation was undertaken in order to detect possible variations in the transmission of benzophenone and related compounds near the melting point.

Isochromatics of benzophenone, desoxybenzoin, dibenzyl ketone, and benzalacetophenone have been studied by the method previously described by the writers.[3] Fig. 1 shows the results obtained for benzophenone. The compound, prepared by D. E. Adelson of the local chemistry department, melted at 47–48°C. As may be seen from the figure a marked decrease in transmission occurs over the range 40° to 50°C, the exact ranges showing only a slight variation with wave-length. The total change in transmission decreases with increasing wave-length. Although the curves shown were obtained with the same sample, similar data were obtained with other samples. The isochromatics for desoxybenzoin (Eastman product, M.P. 61.6°C) are given in Fig. 2. These curves indicate a gradual increase in transmission at temperatures as much as fifteen degrees below the melting point and the usual rapid increase which accompanies melting. The temperature range of increasing transmission varies from nineteen degrees at 1μ to only four and one-half degrees at 9.2μ, an effect indicating that the optical properties of the compound vary more rapidly with temperature in the short wave-length region, an effect also noticed in the study of the liquid crystalline compounds. It will be noticed that the total change in transmission is greatest at short wave-lengths. Although isochromatics for dibenzyl ketone (Eastman) showed a slight decrease (one or two percent) immediately below the melting point, the temperature interval over which the sample could be studied below the melting point was too short to allow any definite conclusions to be drawn. In the case of benzalacetophenone the transmission remained approximately constant in the solid state and increased rapidly at the melting point, the usual result obtained with normal compounds.

In Fig. 3 are shown the spectra of benzophenone, desoxybenzoin, and dibenzyl ketone at the temperatures indicated. For dibenzyl ketone both curves were taken at room temperature, the upper curve showing the transmission of the supercooled liquid and the lower curve showing that of the solid. The same cell was used in obtaining the spectra of both phases of the first two compounds, while different absorbing layers were employed in the case of dibenzyl ketone. It will be seen that the spectra of the solid and liquid phases differ chiefly in background transmission and in the relative intensity of certain bands. The latter effect is especially noticeable in the absorption near 7.7μ and 8.4μ in desoxybenzoin and dibenzyl ketone. Although the C−H bands

[1] J. Errera, Physik. Zeits. **29**, 426 (1928).
[2] L. S. Ornstein and W. Kast, Proc. Farad. Soc. **29**, 939 (1933).
[3] R. Taschek and Dudley Williams, J. Chem. Phys. **6**, 546 (1938).

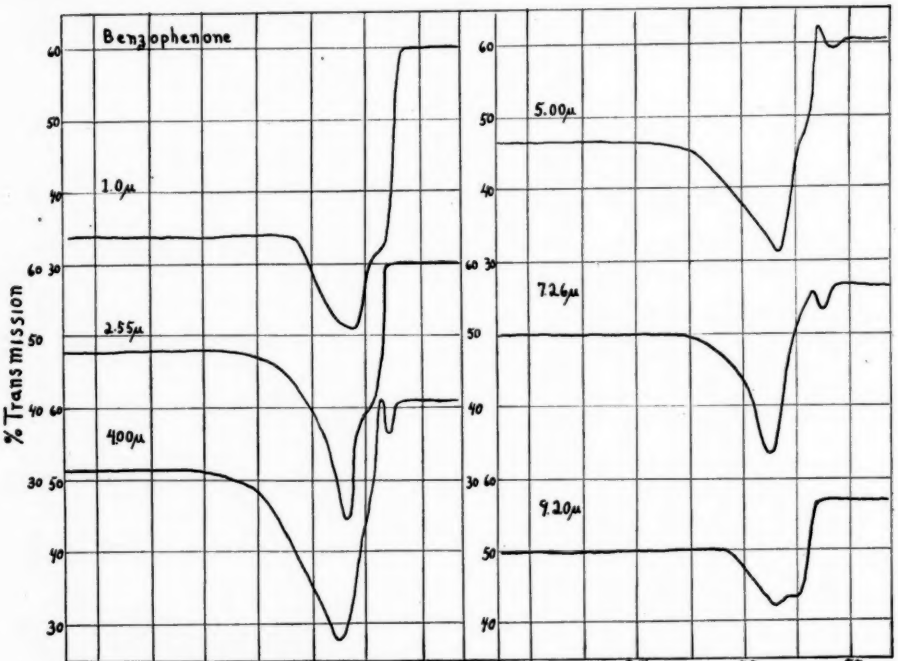

FIG. 1. Isochromatic curves for benzophenone. (Heating; Transmission as a function of temperature.)

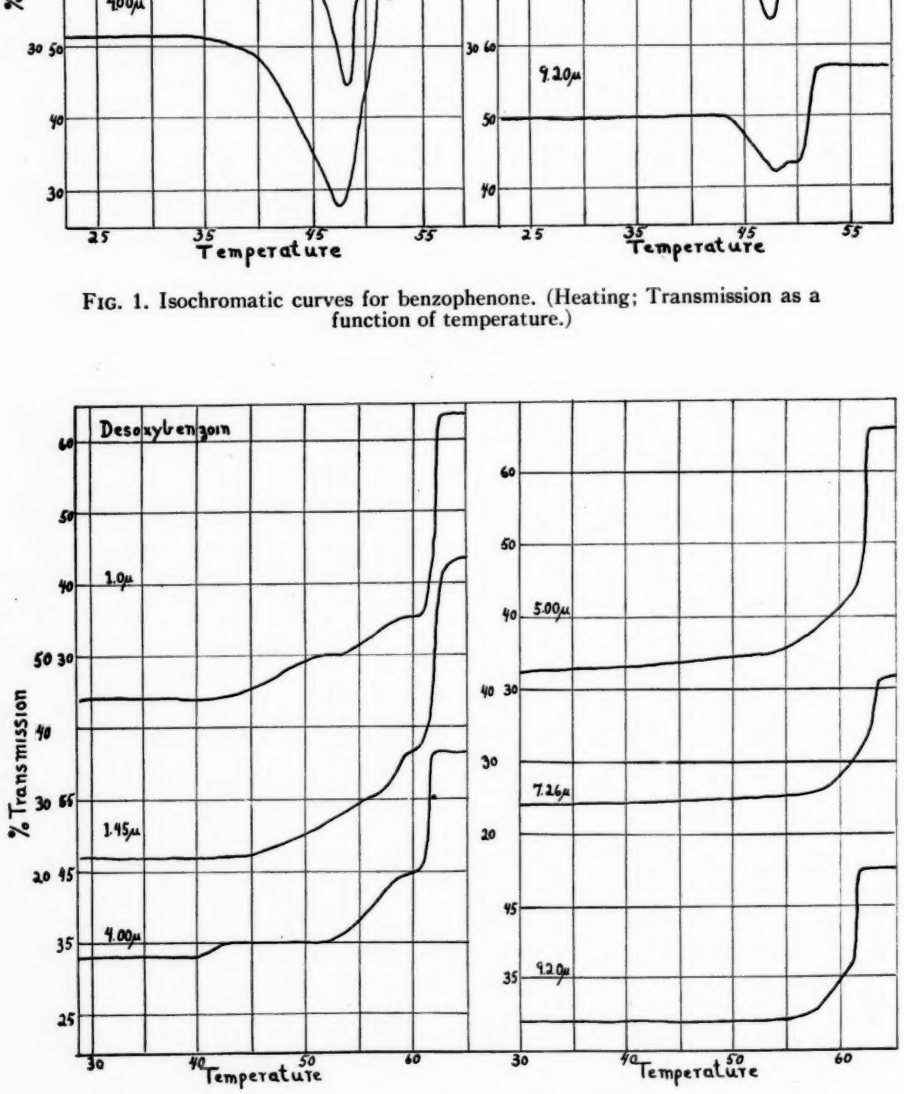

FIG. 2. Isochromatic curves for desoxybenzoin. (Heating.)

in the 3μ region are poorly resolved, it appears that the addition of aliphatic groups causes a shift to longer wave-lengths. The addition of these groups is also accompanied by a marked increase in the intensity of the C=O band at 5.8μ. Krishnamurti[4] has observed a decrease in the Raman frequency of the C=O group of benzophenone on passing from the liquid to the solid state. The present study reveals a similar effect in the case of desoxybenzoin and dibenzyl ketone. The C=C band characteristic of the benzene ring is present near 6.25μ in the spectra of all the compounds studied. The band at 6.9μ in benzophenone and desoxybenzoin shifts to 7.05μ in dibenzyl ketone. The 8μ and 8.7μ bands in the benzophenone spectrum are replaced by complex absorption near 8.3μ in the other compounds. The small side band at 7.7μ in benzophenone apparently is present with increased intensity near 7.7μ in desoxybenzoin and at 7.6μ in dibenzyl ketone. The bands beyond 9μ have counterparts in other aromatic compounds, although the frequencies differ in the various compounds. The band at 10.1μ in desoxybenzoin was not found in the spectra of the other compounds.

The previous infra-red study[3] of compounds known to have an anisotropic liquid phase has shown that the background transmission in the mesophase is different from the transmission of the solid and true liquid phases. The altered transmission of benzophenone and desoxybenzoin at temperatures near their melting points can therefore be interpreted as indicating the existence of an intermediate phase similar to a liquid crystalline phase over a short temperature interval, although similar changes in transmission could probably be produced by polymorphous transitions in the solid. On the basis of their conductivity measurements Ornstein and Kast[2] are inclined to take the former view in the case of benzophenone. However, several polymorphous forms of benzophenone are known and two transition points are listed[5] for the temperature interval in which modified conductivity and transmission are observed. Hauser and Mark[6] report that a crystal of benzophenone 1° below its melting point shows only extremely weak x-ray interference phenomena while still having the appearance of a perfect crystal.

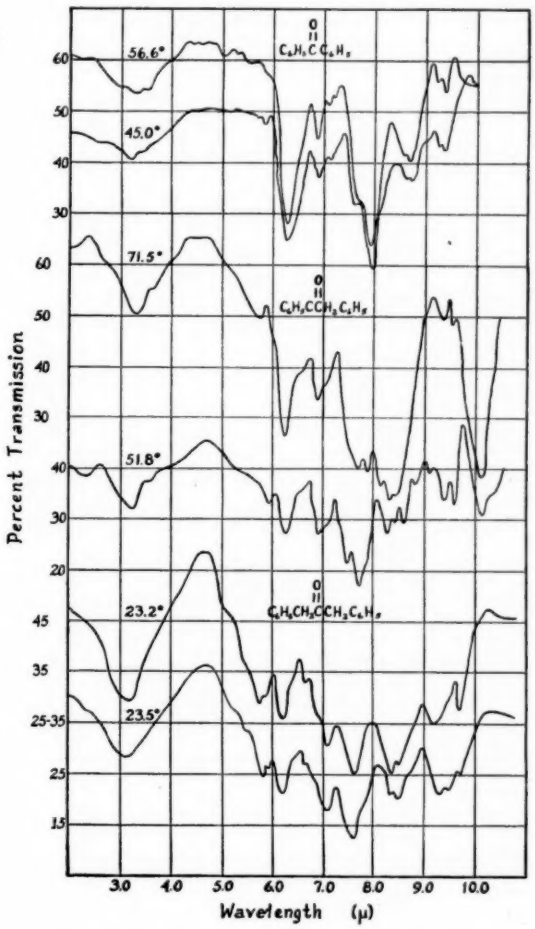

FIG. 3. The infra-red spectra of benzophenone, desoxybenzoin, and dibenzyl ketone.

The results obtained indicate that the present method is a sensitive means of detecting changes in the state of aggregation near the melting point. In the case of benzophenone the changes observed by the present arrangement for measuring transmission are even more pronounced than the variations detected by methods involving conductivity measurements.[2]

[4] P. Krishnamurti, Nature **125**, 463 (1903).

[5] *The International Critical Tables* list the following transition temperatures: −51°C, 26°C, 45 to 48°C, and 49°C.

[6] E. A. Hauser, *Latex* (Chemical Catalog Company, New York, 1930), p. 157.

Intensities of Electronic Transitions in Molecular Spectra

I. Introduction

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The neglected problem of the theory of the absolute intensities of electronic transitions in molecular spectra is discussed. General equations for dipole strength, Einstein coefficients, mean lifetimes of excited states, f values, and so forth, are collected in forms convenient for use in later papers where the theory for various types of transitions will be developed and applied.

1. STATEMENT OF THE PROBLEM

THE problems of the relative intensities of band-lines in a band, and of bands in a band-system, have received a considerable amount of attention, both experimental and theoretical. The problem of the absolute strengths of electronic transitions in molecules, on the other hand, has been studied hardly at all except experimentally.[1, 2] Furthermore, most of the experimental data are on complex molecules in the liquid state or in solution,[3] whereas quantitative data on simple molecules in the vapor state, which would be particularly useful for comparison with theory, are rather scarce.

A systematic development of the theory and its systematic application to existing and new data appear to have fruitful possibilities. Such a development should be valuable particularly for the understanding of molecular spectra and structure in simple and complicated molecules, and also as a step toward the quantitative determination of molecular concentrations in celestial objects.[1, 4] The theoretical interpretation of absolute intensity data should be especially useful in the case of continuous spectra, where information about electronic states and molecular constants obtainable from band-structure analysis is lacking.

The present paper is a general discussion of the theoretical problem of absolute intensities, with notation, a collection of relevant general formulas, and so on. The next paper of the series contains a study of an interesting special class of rather strong electronic transitions. In later papers, this class of transitions, and others, will be considered more in detail.

2. GENERAL CONSIDERATIONS

When an electron jump occurs in an atom, we get a single usually narrow line. When an electron jump occurs in a molecule, we get a spectrum which usually extends over a broad range of wave-lengths; this may consist of a band-system, i.e., a number of bands each made up of narrow lines, or of a broad region of continuous absorption, or of bands *and* continuum. As is well known, bands occur when both initial and final states are discrete vibration-rotation states of a stable electronic state, continuum when either initial or final state or both have energy in excess of that required for dissociation.

Our basic procedure will be to treat the *total spectrum* associated with a single electronic transition in a molecule like the single line associated with a single electronic transition in an atom. We may liken the molecular spectrum if it is continuous to a very broad atomic line; if it

[1] Preliminary reports on the present work were given at the 1938 Washington meeting of the National Academy of Sciences, Science, **87**, 427 (1938); and at a conference on molecular spectra at the Yerkes Observatory in June, Astrophys. J. to be published.

[2] B. Mrowka, Zeits. f. Physik **76**, 300 (1932); **84**, 448 (1933), has made approximate quantum-mechanical calculations for certain electronic transitions in H_2. These will be considered in a later paper. H. M. James has made exact calculations on absolute strength for the important transition $(\sigma_g 1s)(2s\sigma_g)$, $^3\Sigma^+_g \rightarrow (\sigma_g 1s)(\sigma_u 1s)$, $^3\Sigma_u^+$ in H_2 (soon to appear in the *Physical Review*). The writer is not aware of other theoretical work.

[3] N. Q. Chako, J. Chem. Phys. **2**, 644 (1934) has surveyed the data on organic compounds.

[4] Currently, f values which may often be greatly in error are assumed in estimating molecular concentrations from band spectra appearing in celestial objects. See O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 439 (1938), for experimental f determination in the case of the OH bands, and for discussion of the astrophysical application.

has band structure, to an atomic line having fine structure. Just as the strength of a single atomic line is obtained experimentally from (and is defined by) the integral of intensity over the whole width of the line, so the strength of a molecular electronic transition can be obtained experimentally from, and be defined by, the integral of intensity over all the band-lines and the whole of the continuum belonging to the particular electronic transition.

The procedure outlined in the foregoing paragraph is justified in the following way. If the nuclei of a molecule could be held stationary in some fixed configuration (for example, the equilibrium configuration), then we would *really* have a single line for each electronic transition, just as for an atom. If now we let the molecule vibrate and rotate not too violently, we know from the theory of molecules that this affects only slightly the environment acting on the electrons, and it is clear that the quantitative strength of the electronic transition should be altered very little (see later paragraph for exact definition of strength). However, that strength is no longer concentrated in a single line, but scattered over many lines or over a broad continuum.

For an assemblage of molecules forming a gas or vapor, this scattering of strength occurs for two reasons. (1) The various molecules are distributed over a variety of initial states having various vibrational and rotational quantum numbers but all belonging to the one initial electronic state under consideration. (2) Each individual molecule, although it is initially in one definite vibrational-rotational state, has in general a variety of possible choices among final vibrational-rotational states (including continuous unquantized states) belonging to the single final electronic state under consideration. On the basis of the discussion in the preceding paragraph we can state that for a single molecule, whatever its initial vibration-rotation level, the *sum of the strengths* of all lines (plus integral of strength over any continuum) must be practically the same as the strength of the hypothetical single line which we would have if the nuclei could be held stationary. As a corollary, the sum of the strengths of lines and continuum arising from a given initial level is practically independent of the vibrational and rotational quantum numbers of that level. This is analogous to the familiar theorem for atoms that if we consider the Zeeman components of an atomic line, the sum total intensity of all those Zeeman components which start from a particular Zeeman level of the initial state is the same for all the possible initial Zeeman levels, that is, is independent of the initial M value.

Returning to items (1) and (2) of the preceding paragraph, we note that two methods are available for obtaining experimentally the *total strength per molecule* of a molecular electronic transition. (A) We may deal with a particular initial vibration-rotation state (cf. Oldenberg and Rieke[4]), and measure the strengths of all the lines arising from this; dividing the sum of these strengths by the initial population of the given initial vibration-rotation state, we get the desired total strength per molecule. We can check this by doing the same thing for other initial states. This method can be used only for spectra consisting of discrete bands with lines which can be identified and properly measured; for a continuous spectrum, the observed intensity of course cannot be divided up experimentally between individual initial vibration-rotation levels. Further, the method can be used only if we know the initial populations of the various vibration-rotation states; this limits us to *absorption spectra*, and to bands whose structure has been analyzed. (B) We may deal with the totality of initial vibration-rotation states, and measure the total strength of all the lines and/or continuum; dividing this result by the total population of all the initial states, and relying on the theorem that the sum-of-strengths is practically the same for each and every initial vibration-rotation state, we get the desired total strength per molecule for the given electronic transition. This method is admirably suitable for continuous absorption spectra. It is possible but experimentally impracticable for discrete absorption spectra. Discrete spectra can, however, sometimes be so blurred out by using gas at high pressure that they are practically continuous, so that method (B) is rendered feasible.[5]

[5] Cf. the application of this method to I_2 vapor by E. Rabinowitch and W. C. Wood, Trans. Faraday Soc. **32**, 540 (1936).

In connection with method (B), it is desirable to note that the measured total strength should ordinarily be practically independent of the temperature of the absorbing gas. Change of temperature merely redistributes the molecules among the rotational-vibrational levels, and this, according to preceding considerations, should not appreciably change the total strength of absorption per molecule.

The total absorption strength of an electronic transition can be measured with especial convenience in the liquid state or in solution. Any fine structure which may be present in the vapor is blotted out. But caution must be used in comparing such data with theoretical calculations made for isolated molecules, since the total strength of a given transition may be considerably altered in liquid or solution as compared with vapor.[3]

In order to justify the foregoing sum and independence rules more clearly and also to qualify them slightly, we may to a good approximation write any molecular wave function in the following usual form:

$$\Psi \approx \Psi_{el}(q, Q)\Psi_{nu}(Q, \theta). \qquad (1)$$

Here q refers to the electronic coordinates, measured relative to a system of axes fixed in the molecule, Q and θ to the nuclear vibrational and rotational coordinates. For a diatomic molecule, Q becomes the single coordinate r measuring the distance between the two nuclei. $\Psi_{el}(q, Q)$ is a solution of the electronic Schrödinger equation for the electrons in the field of force of a fixed nuclear configuration Q. The form of Ψ_{el} depends on the parameters Q, but so long as the *average* values of these in $\Psi_{nu}(Q, \theta)$ do not depart very much from their equilibrium values, this variation of the form of Ψ_{el} can usually be neglected for our purposes. Since the vibrational-rotational states initially occupied, especially in the case of absorption spectra, ordinarily satisfy the foregoing condition on the average values of Q, we see that Ψ_{el} of the initial electronic state behaves practically the same for all appreciably populated initial vibration-rotation states. In view of the Franck-Condon principle, the effective Ψ_{el} for those vibration-rotation (or continuum) states of the *final* electronic state which make appreciable contributions to the total intensity is likewise nearly independent of the particular detailed final state. Since the total strength of the electronic transition for fixed nuclei depends on an integral of the type $\int \Psi_{el_m}{}^*(\Sigma_i r_i)\Psi_{el_n} d\tau$, it is clear that this strength should be nearly independent of the initial state of vibration and rotation, and practically equal to the strength calculated from the above integral for nuclei fixed at proper Q values.[6]

[6] For an explicit justification of the theorem that the *total strength* is not much affected by the fact of distribution of the intensity over a range of final states, compare J. H. Van Vleck, Phys. Rev. **33**, 479 (1929), especially Eqs. (23), (24), after substituting electric moment for angular momentum matrix components; also Proc. Nat. Acad. Sci. **15**, 754 (1929). For some relevant calculations, cf. also Mrowka, reference 2.

In special cases, there can be pronounced departures of total strength from that computed for nuclei fixed at equilibrium distances. Such cases must be looked out for whenever, for any reason, large amplitude vibrations occur; in particular, when there are vibrations of unusually low frequency, e.g., torsional vibrations. Further, the present discussion is inapplicable to transitions which violate electronic selection rules that hold for the equilibrium configuration of the molecule; such transitions can occur,[7] because of the interaction of electronic and nuclear motions, but with low intensity, and only in polyatomic molecules.

3. Notation and Useful Formulas

It will be helpful to set down here such general formulas and notation as may be needed in later papers.

Experimentally, we shall deal almost entirely with absorption spectra. In general, we shall use the absorption coefficient k_ν defined by the equation

$$I_\nu = I_\nu{}^0 e^{-k_\nu l}, \qquad (2)$$

where l is the light path expressed in cm of gas at 0°C and 1 atmosphere pressure, and ν, *as always in the following*, indicates spectral location in cm^{-1}.

As experimental measures of the total strength of an electronic transition, quantities such as $\int k_\nu d\nu$ and $\int k_\nu d\nu/\nu$ will be found useful, the integration being carried across the whole range of spectrum belonging to the transition in question. In the case of continuous spectra, with which we shall mainly deal, k_ν for a single electronic transition possesses a single maximum, whose wave number we shall designate as ν_{max}. For rough characterization of an absorption continuum, k_{max}, ν_{max}, and the two wave number values $\nu_{\frac{1}{2}max}$, at which k_ν is half of k_{max}, are very useful. The distance between the two $\nu_{\frac{1}{2}max}$ points will be called $\Delta\nu$. As a convenient rough

[7] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **21B**, 410 (1933).

approximation, we have

$$\int k_\nu d\nu \approx k_{\max}\Delta\nu. \tag{3}$$

A number of interconnected formulas useful for later reference will now be given.[8] The *dipole strength* $D'_{,,}$ for the transition connecting two orbital electronic wave functions ψ' and ψ'' (where the meaning of the superscripts is that ψ' has the higher and ψ'' the lower energy), may be defined as

$$D'_{,,}\equiv Q'_{,,}{}^2, \quad \text{with} \quad Q'_{,,}=\int \psi'^*(\sum_i q_i)\psi'' d\tau. \tag{4}$$

Here q_i is one coordinate ($q=x$, or y, or z) of the ith electron, the coordinate axes being fixed in the molecule, with the z axis along the principal axis of symmetry if there is such an axis. Instead of x and y, the choices $x+iy$ and $x-iy$ are of course often useful. The ψ's are to be chosen as described in the second following paragraph.

The Einstein probability coefficients per molecule, $A'_{,,}$ (total spontaneous emission probability) and $B''_{,}$ ($B''_{,}\rho_\nu$ being the total absorption probability in the presence of radiation of density ρ_ν ergs/cc/cm^{-1}), are then given by

$$A'_{,,}=[64\pi^4\nu^3e^2/3h]G''D'_{,,}, \tag{5}$$

$$B''_{,}=[8\pi^3e^2/3h^2c]G'D'_{,,}. \tag{6}$$

In Eqs. (5) and (6), each G represents the number of suitable final orbital ψ's, belonging to the same final energy level, with which *any one* suitable orbital ψ of the initial energy level can combine.

By "suitable" orbital ψ's are meant orbital ψ's which fulfill the following conditions: (1) for each electronic state they are mutually orthogonal and normalized; (2) they are all chosen in the simplest possible way with respect to the axes x, y, z; (3) real ψ's are chosen if x, y, z are used as coordinates, complex ones if $x+iy$, $x-iy$, z are used. For the most part, we shall use *real* ψ's. For a given electronic state we can then employ the designation ψ if the state has no orbital degeneracy, the designations ψ_x and ψ_y if the state has twofold orbital degeneracy, ψ_x, ψ_y, ψ_z if it has threefold orbital degeneracy. Electronic states with greater than threefold orbital degeneracy are not expected in molecules.[9] Correspondingly, the G's in Eqs. (5) and (6) are never larger than three.

Spin structure, if it occurs, can be treated for our purposes in practically the same way as vibrational and rotational structure. That is, it can be merely ignored in our theoretical formulas, Eqs. (4)–(6) *et seq.*, while on the experimental side it is only necessary to be sure to sum or integrate over all of the spectrum corresponding to different spin states. Or in the case of an initial state containing widely separated spin components so that the total strength of the spectrum from each can be measured separately, the result from any one component is acceptable if due allowance is made for initial population; the total strength per molecule should be the same for each initial spin component.

As has been mentioned already, our procedure cannot be used directly for transitions which are forbidden by electronic selection rules. Under this heading should be included transitions in which the resultant spin quantum number changes (intersystem transitions). All forbidden transitions must be treated as perturbation problems; the observed intensity of the forbidden transition may be regarded as stolen from the intensities of allowed transitions, as a result of perturbation of the initial and/or final energy level by levels connected with allowed transi-

[8] Cf., e.g., H. Bethe, *Handbuch der Physik*, Vol. 24/1 (J. Springer, Berlin, 1933), pp. 57, 430–1, 435, 443, etc. Eqs. (5), (6), (8), (9) for molecular electronic transitions can be obtained by considering first the $A'_{,,}$ or f''' formula for a transition between a single upper-state and a single lower-state wave function, then (for degenerate electronic states) summing over all final-state and averaging over all initial-state wave functions (cf. Bethe, *l.c.*, p. 435, on the corresponding procedure for atoms). Note that the f''' that we need is a *mean* f corresponding to randomly-oriented molecules (cf. Bethe, p. 435). [The one-dimensional f given by Bethe (*l.c.*, p. 431, Eq. (38·14)) has a coefficient three times as large, because it corresponds to x-polarized light and an x-oriented linear oscillator.]

[9] Cf. R. S. Mulliken, Phys. Rev. **43**, 279 (1932). Strictly speaking, degenerate electronic states do not give stable equilibrium configurations except for linear molecules (H. A. Jahn and E. Teller, Proc. Roy. Soc. **161A**, 220 (1937); H. A. Jahn, Proc. Roy. Soc. **164A**, 117 (1938)); but for our purposes this usually makes no difference. For example, if absorption, allowed by electronic selection rules, occurs starting from a stable nondegenerate electronic state and going to an upper state which would have threefold degeneracy if the initial equilibrium symmetry were preserved, the over-all intensity of the transition is not appreciably affected if the actual equilibrium symmetry is different in the upper state.

tions. No simple general formulas can be given to cover such cases; they must be considered more or less individually. In certain types of intersystem transitions, however, simple formulas can be obtained; some of these will be treated in a later paper on halogen and halide molecules.

The meaning of Eqs. (4)–(6) can be made clear by discussing a few examples chosen from the important case of diatomic or linear molecules. There all electronic transitions can be divided into *parallel-type transitions*, where $q_i = z_i$ in Eq. (4), and *perpendicular-type transitions*, where $q_i = x_i$ or y_i (or $x_i \pm iy_i$) in Eq. (4); the z axis is along the line joining the nuclei. In perpendicular-type transitions, *either* x_i or y_i may be used in Eq. (4), since the directions x and y are physically equivalent. (In the following, we shall use the real coordinates x_i, y_i, and real wave functions.)

For parallel-type transitions, which occur when $\Delta\Lambda = 0$ (e.g. $\Sigma \rightarrow \Sigma$ or $\Pi \rightarrow \Pi$ and so on), we always have $G'' = G' = 1$ in Eqs. (5) and (6). In a $\Sigma \rightarrow \Sigma$ transition, for example, there is only one initial and one final wave function, so, of course, the G's are both one. In a $\Pi \rightarrow \Pi$ transition, each electronic energy level has twofold degeneracy. We still have $G' = G'' = 1$, however, because whichever one of the two initial wave functions may happen to be occupied by a given molecule, a transition can take place from it only to one of the two final wave functions. Thus if the four wave functions are designated ψ'_x, ψ'_y, ψ''_x, and ψ''_y, it can be shown that only the transitions $\psi'_x \rightleftarrows \psi''_x$ and $\psi'_y \rightleftarrows \psi''_y$ are allowed.

For perpendicular-type transitions, which occur when $\Delta\Lambda = \pm 1$, we may have $G'' = 1$, $G' = 2$, or $G'' = 2$, $G' = 1$, or $G' = G'' = 1$. $G'' = 1$, $G' = 2$ occurs in the very common case of a Π upper and a Σ lower state; $G'' = 2$, $G' = 1$ for a Σ upper and a Π lower state. $G' = G'' = 1$ occurs for all other types of transitions ($\Delta \rightarrow \Pi$, $\Pi \rightarrow \Delta$, and so on). Let us further consider the case of a Π upper and Σ lower state. In emission, either of two initial wave functions ψ'_x or ψ'_y is available, but there is only *one final* wave function ψ'', so $G'' = 1$ in Eq. (5). In Eq. (4), q_i is x_i or y_i according as ψ'_x or ψ'_y is used, but D has the same value in both cases. In absorption, only one initial wave function ψ'' is available, but from here a jump may occur to either of the two equivalent final functions ψ'_x and ψ'_y, hence $G' = 2$ in Eq. (6), and the total transition probability is then doubled because of the degeneracy in the upper state. The case of a Σ upper and Π lower state shows reversed relations, the transition probability being doubled in emission instead of in absorption.

As we have just seen, all electronic transitions in diatomic and linear molecules are divided into two classes, parallel-type (z polarization) and perpendicular-type (x, y polarization). A similar division exists for molecules of several symmetry types characterized by a single principal axis of symmetry, except, however, that transitions between two (here twofoldly) degenerate states have in some cases simultaneously parallel and perpendicular polarization.[9] Eqs. (4)–(6) would then have to be used with caution. The D of Eq. (4) would now be different for the parallel and perpendicular components of the transition, and Eqs. (5)–(6) should be first applied to each component separately. In other molecules of high symmetry, similar cases would need to be similarly treated. However, a theorem of Jahn and Teller[9] indicates that the cases just considered, giving rise to transitions with mixed polarization, are hardly to be expected in practice. Hence Eqs. (4)–(6) should in practice be applicable without reservation to all molecular electronic transitions not violating electronic selection rules.

Eqs. (4)–(6) differ somewhat from the corresponding equations for atoms, where degeneracies higher than threefold are common. The ratio $A'_{,,}/B''_{,,}$, however, is equal there as here to $(8\pi\nu^3/hc)(g''/g')$, where the g's are the statistical weights of lower and upper electronic states; this relation is the universally valid one for the Einstein coefficients $A'_{,,}$ and $B''_{,,}$. Although G'' and G' in Eqs. (5)–(6) are not statistical weights, their ratio G''/G' is always equal to g''/g'.

We next consider formulas connected with dispersion. For the index of refraction N of a gas, approximately,

$$N - 1 = (e^2 n/2\pi mc^2) \sum_j f_{ij}/(\nu_{ij}^2 - \nu^2), \qquad (7)$$

where n = number of molecules per cc and the summation is over all excited states j (including

continuum states) to which transitions from the normal state i can occur; f_{ij} is the effective *number of dispersion electrons*, or *mean oscillator-strength*, of the transition $i \rightarrow j$. Between any f_{ij}, which we shall call $f''_{,}$ and the corresponding B'', there exists the relation

$$f''_{,} = (mhc^2\nu''_{,}/\pi e^2)B''_{,} \qquad (8)$$

and so, using Eqs. (6), (8), the total integrated f'', over the broad absorption band or spectrum of any one molecular electronic transition is

$$f''_{,} = (8\pi^2 mcG'/3h)\nu''_{,}D'_{,} = 1.096\times 10^{11} G'\nu''_{,}D'_{,}. \qquad (9)$$

Conversely,

$$D'_{,} = (3h/8\pi^2 mcG')f''_{,}/\nu''_{,} = 0.912\times 10^{-11} f''_{,}/G'\nu. \qquad (10)$$

Eq. (9) will often be used in subsequent papers to calculate f values based on an experimental (or theoretical) ν combined with a D calculated theoretically using Eqs. (4). Eq. (10) may be used to calculate experimental D values from experimental f values, the latter based on dispersion data formulated as in Eq. (7).

Strictly speaking, the quantities $\nu''_{,}/B''_{,}$, $\nu''_{,}/D'_{,}$, and $f''_{,}/\nu$ in Eqs. (8)–(10) should be replaced by integrals over a range of ν (cf. Eqs. (17)–(21) below). As a close approximation, however, we can use Eqs. (8)–(10) with ν set equal to ν_{max} or to $\bar{\nu}$ (where $\bar{\nu}$ is a suitable average value of ν). This procedure will prove entirely adequate for our purposes and will be followed in subsequent papers, since our theoretical values of D will be calculated only in rough approximation.

Besides $A'_{,}$, $B''_{,}$, and $f''_{,}$, the *average life* τ_j of an excited molecule in a definite excited electronic state j can be calculated theoretically. We have in general,

$$\tau_j = 1/\sum_i A^j{}_i. \qquad (11)$$

If the ν_{ij}'s are known and the D's can be calculated in Eq. (5), τ_j can be calculated. In the important special case that the only lower state i with which state j combines is the normal state, we have $\tau_j = 1/A^j{}_i$; we have then, among others, the relation

$$\tau_j = (mc/8\pi^2 e^2)(g_j/g_i)(1/f^i{}_j\nu_{ij}{}^2). \qquad (12)$$

We turn next to relations between experimental absorption data and the quantities A, B, f, and D. We must now specifically recognize the fact that for molecular electronic transitions these quantities do not correspond to sharp lines, but really represent integrals over a range of ν, thus:

$$B \equiv \int (dB/d\nu)d\nu; \quad f \equiv \int (df/d\nu)d\nu; \qquad (13)$$

and

$$D \equiv \int (dD/d\nu)d\nu.$$

The quantities $dB/d\nu$, $df/d\nu$, and $dD/d\nu$ are all functions of ν. They can be determined experimentally from measurements of the absorption coefficient k as a function of ν. Their theoretical calculation would involve a study of the ψ_{nu} factor in Eq. (3). But in the present papers it is just this problem in which we are *not* primarily interested. While recognizing their character as integrals over ν, we shall work so far as possible with the integrated quantities B, f, and D.

From the easily verified relation[10]

$$dB/d\nu = (1/nh)k_\nu/\nu, \qquad (14)$$

combined with Eqs. (6), (12), we have

$$D'_{,} = (3hc/8\pi^3 ne^2 G')\int k_\nu d\nu/\nu = (3.83\times 10^{-19}/G')\int k_\nu d\nu/\nu, \qquad (15)$$

and

$$\int k_\nu d\nu = (8\pi^3 ne^2 G'/3hc)\int (dD'_{,}/d\nu)\nu d\nu. \qquad (16)$$

In comparing theory with experiment, Eqs. (4), (15) should be particularly useful, D calculated theoretically using Eq. (4) being compared with D obtained from Eq. (15) using experimental data on k_ν.

Instead of Eqs. (8)–(10), which tacitly assume a single definite ν, it is clear that we should write, in view of Eqs. (13),

[10] For derivation of Eq. (19), cf. R. Ladenburg, Verh. d. D. Phys. Ges. **16**, 769 (1914); Zeits. f. Physik **4**, 451 (1921); cf. also R. Ladenburg and C. C. Van Voorhis, Phys. Rev. **43**, 320 (1933).

$$(df''_{,}/d\nu)=(mhc^2/\pi e^2)\nu dB''_{,}/d\nu \quad (17)$$

$$=(8\pi^2mcG'/3h)\nu dD'_{,,}/d\nu. \quad (18)$$

From these we get[10] by integration, using Eqs. (13), (14),

$$f''_{,}=(mc^2/n\pi e^2)\int k_{\nu}d\nu=4.20\times10^{-8}\int k_{\nu}d\nu, \quad (19)$$

$$f''_{,}=(8\pi^2mcG'/3h)\int(dD'_{,,}/d\nu)\nu d\nu$$

$$=1.096\times10^{11}G'(dD'_{,,}/d\nu)\nu d\nu, \quad (20)$$

$$D'_{,,}=(3h/8\pi^2mcG')\int(df''_{,}/d\nu)d\nu/\nu. \quad (21)$$

Eq. (19) could be used to calculate experimental f's from experimental k_{ν} data.

Eqs. (20), (21) require a knowledge of $dD/d\nu$ or $df/d\nu$ as a function of ν. If this knowledge is not available, Eqs. (9), (10) can be used instead; as a matter of fact, Eqs. (9)–(10) will be entirely adequate for our purposes, as was explained above.

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Intensities of Electronic Transitions in Molecular Spectra

II. Charge-Transfer Spectra

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Two related types of high intensity molecular spectra are discussed. These are designated as charge-resonance spectra and charge-transfer spectra. In the molecular orbital approximation, both these types usually involve transfer of one electron from a bonding to the corresponding antibonding molecular orbital. In the atomic orbital approximation, charge-resonance spectra involve a transition from a symmetrical to a corresponding antisymmetrical state, the wave function of each of these two states being a linear combination of two wave functions representing two hypothetical states of a molecule that are equivalent or nearly so but different in charge distribution. Charge-transfer spectra in the atomic orbital approximation involve a transition from a state having a non-ionic to one having an ionic wave function ($N\rightarrow V$ transition). Theoretical equations for dipole strengths and f values for both these types are given, in each case calculated according to each of the two approximations. The equations are very simple, the dipole strength being proportional to the distance across which the charge resonates or is transferred.

Examples of charge-resonance spectra in H_2^+, O_2^+, and NO are cited, and $N\rightarrow V$ (charge-transfer) transitions in the spectra of the molecules H_2, O_2, C_2H_4, C_6H_6, and the halogens are discussed. Although experimental data are scanty, they appear to be in harmony with the theory. For the O_2 Schumann-Runge bands, where f is accurately known experimentally, its value is intermediate between the values calculated theoretically according to the two approximations. A suggestion is made to explain Carr and Stücklen's result of progressive broadening toward longer wave-lengths in the $N\rightarrow V$ spectrum as radicals are substituted for H atoms in C_2H_4. The $^1A_{1g}\rightarrow{}^1E_{1u}$ transition in C_6H_6 calculated by Sklar and identified by him with bands near and below λ2000 is here concluded to be of the $N\rightarrow V$ class. In connection with the theory of light absorption in organic compounds, it will be shown in later papers that intense transitions in the visible and ordinary ultraviolet probably can be accounted for in a large proportion of cases (including dyes) as charge-transfer ($N\rightarrow V$) spectra, or, in part, as charge-resonance spectra. The existence of spectra of the charge-resonance type in certain kinds of dyes has already been recognized and very briefly discussed by Pauling in the new edition of Gilman's *Organic Chemistry*.

1. INTRODUCTION

THE writer concluded in earlier papers[1, 2, 3] that there probably exists in the spectra of diatomic molecules a class of parallel-type electronic transitions ($\Delta\Lambda=0$) of high intrinsic intensity, characterized in Heitler-London approximation by a non-ionic lower state and an ionic upper state. In the examples considered, both states were $^1\Sigma^+$, the lower being the normal state ("N") and the upper a state called "V."

[1] R. S. Mulliken, Phys. Rev. **46**, 549 (1934).
[2] R. S. Mulliken, Phys. Rev. **50**, 1017, 1028 (1936).
[3] The conclusion is clearly stated in Phys. Rev. **51**, 315 (1937), postulate 1.

The present work arose from a desire to give definite theoretical justification to the idea that such non-ionic→ionic $N \rightarrow V$ transitions should really be expected to have high intensity. A very simple calculation immediately showed that the idea was correct, and also suggested other interesting possibilities.

Roughly speaking, molecular electronic transitions can be divided into Rydberg series transitions and sub-Rydberg transitions. The former are rather closely analogous to atomic transitions, and should for the most part obey similar intensity rules, the lowest members of such series being expected generally to be fairly intense. In most commonly observed molecules the Rydberg transitions occur in the vacuum ultraviolet, but in some molecules, e.g., the Li_2 type, they occur at longer wave-lengths. Sub-Rydberg transitions occur for the most part at lower frequencies, and comprise a large part of the ordinary visible and ordinary ultraviolet band spectra. They are generally of much lower intensity than the conspicuous Rydberg transitions and correspond to transitions that would be forbidden in atoms,—that is to say, if the molecule could be gradually separated into atoms, a sub-Rydberg transition would gradually get weaker and finally disappear when the separation was complete. Details will be given in later papers. Although sometimes it is hard to draw a sharp line, sub-Rydberg states may generally be defined as those molecular states derivable by combining configurationally unexcited atoms or ions,—Rydberg states, as states derived using one configurationally excited atom. "Configurationally excited" means excited to a state not having the same electron configuration as the normal state.

The class of $N \rightarrow V$ transitions belongs among the sub-Rydberg transitions, but is unusual in its high intensities; also, the transitions generally have rather high frequencies, approximating those of the lowest Rydberg series members. In some cases the state V may be classed more or less properly both with the Rydberg and with the sub-Rydberg states.

In investigating the theory, it proves that the $N \rightarrow V$ type is one of several related varieties of highly intense transitions in diatomic and polyatomic molecules. These types all have in common that either within the individual wave functions, or else by the transition, there is exchange or transfer of an electron or electrons between atoms in a molecule. This characteristically molecular type of spectra has of course no counterpart in the spectra of single atoms. More or less similar spectra are known, however, for crystals.

The discussion so far has been based on the point of view of the atomic orbital approximation or generalized Heitler-London method. The same transitions show equally characteristic features from the molecular orbital point of view. They are then found to represent jumps of an electron from a bonding to a corresponding antibonding molecular orbital, or vice versa.

In order to save space, we shall *from now on use the abbreviations* AO for "*atomic orbital*" or "*atomic orbital approximation*," etc., and MO for "*molecular orbital*" or "*molecular orbital approximation*," etc.

Recapitulating, our class of intense sub-Rydberg transitions has the following distinctive characteristics: (1) by the AO approximation it involves resonance or transfer of an electron between two atoms; (2) by the MO approximation, it involves transfer of an electron *between a bonding and a corresponding antibonding* MO. In short: (1), atom A↔atom B; (2) bonding ↔antibonding. Finally, (3), in diatomic and linear molecules, these transitions all have $\Delta\Lambda = 0$ (parallel-type transitions).

It is found also that similar transitions involving simultaneous resonance or transfer of two or more electrons (in the AO approximation) can occur with considerable intensity.

In the following sections we shall outline the theory for the main varieties of charge-transfer spectra in homopolar diatomic molecules, discussing a few diatomic and simple polyatomic examples, but reserving a fuller discussion, including also heteropolar molecules, for later papers.

2. One-Electron-Resonance Spectrum in H_2^+

As the prototype of charge-resonance spectra we may take a certain transition in H_2^+. Consider the absorption transition from the lowest or "N" (stable) to the second (unstable) elec-

tronic state of H_2^+, which we may call "*E*." According to the atomic or Heitler-London viewpoint, the wave function of state *N* can be approximated[4] by a *symmetrical* and that of state *E* by the *corresponding antisymmetrical* linear combination of two equivalent atomic wave functions corresponding to H^+H and HH^+. More precisely,

$$\left.\begin{aligned}\Psi_N &\approx (1s_A+1s_B)/2^{\frac{1}{2}}(1+S)^{\frac{1}{2}},\\ \Psi_E &\approx (1s_A-1s_B)/2^{\frac{1}{2}}(1-S)^{\frac{1}{2}},\end{aligned}\right\}(1)$$

where *B* and *A* refer to the left- and right-hand H atoms, and *S* is the nonorthogonality or overlapping integral:

$$S=\int(1s_A)(1s_B)dv. \qquad (2)$$

In Eqs. (1), (2), the symbol $1s$ is used for simplicity to designate the corresponding atomic orbital.

It is to be noted that Eqs. (1) give an approximation which is very good at large r values (r=internuclear distance) but is rather rough at actual molecular distances, and which becomes worthless as $r\to 0$. The wave functions Ψ_N and Ψ_E can be shown to be respectively of the types $^2\Sigma^+_g$ and $^2\Sigma^+_u$. For the transition $^2\Sigma^+_g\to{}^2\Sigma^+_u$, the selection rules ($\Delta\Lambda=0, \pm1$, $g\leftrightarrow u$) are satisfied. Here $\Delta\Lambda=0$, so we have a parallel-type transition.

From the MO viewpoint, *N* is a state containing one electron in a MO which we call σ_g1s and which is a *bonding* orbital, while state *E* has one electron in an antibonding MO σ_u1s. These MO's can be obtained to a high degree of approximation by solving the one-electron Schrödinger equation for H_2^+, but their forms cannot be given accurately by simple expressions. Instead, we shall use an approximation. Since in the present one-electron case $\Psi_N\equiv\sigma_g1s$ and $\Psi_E\equiv\sigma_u1s$, we may use Eqs. (1) to get the following approximate expressions:

$$\left.\begin{aligned}\sigma_g1s &\approx (1s_A+1s_B)/2^{\frac{1}{2}}(1+S)^{\frac{1}{2}},\\ \sigma_u1s &\approx (1s_A-1s_B)/2^{\frac{1}{2}}(1-S)^{\frac{1}{2}}.\end{aligned}\right\}(3)$$

[Classification symbols (σ_g1s, σ_u1s) are here again used to designate orbital wave functions.]

In Eqs. (3), each MO is now roughly approximated as a simple *linear combination of atomic orbitals* (LCAO). It may be emphasized again,[5] here, that the LCAO type of approximation for MO's, while very useful for the qualitative purpose of classifying them as bonding or antibonding, and for rough calculations, should not be taken as primary or as directly fundamental for their definition.[5]

Summarizing, the transition $N\to E$ may be described as follows:

$$\left.\begin{aligned}&N\,{}^2\Sigma^+_g\to E\,{}^2\Sigma^+_u,\ \Delta\Lambda=0,\text{ parallel-type transition}\\ &\text{MO viewpoint: }\sigma_g1s\to\sigma_u1s,\text{ bonding}\to\text{antibonding}\\ &\text{Atomic viewpoint: symmetrical in nuclei}\to\text{antisymmetrical in nuclei.}\end{aligned}\right\}(4)$$

We now proceed to calculate the strength of the transition. For the absorption probability coefficient, we may use Eqs. (4), (6) of the first paper of this series (Paper I).[5a] The main task is the calculation of *Q* of Eq. (I, 4), i.e., of Eq. (4) of Paper I. [*Hereafter Paper* I *will be referred to simply as* I.] Using Eqs. (I, 4) and (1), we get

$$\left.\begin{aligned}Q=\int\Psi_N z\Psi_E dv &\approx [\int 1s_A z 1s_A dv\\ &\quad -\int 1s_B z 1s_B dv]/2(1-S^2)^{\frac{1}{2}}\\ &=(z_A-z_B)/2(1-S^2)^{\frac{1}{2}}.\end{aligned}\right\}(5)$$

Here the coordinate *q* of Eq. (I, 4) is taken as *z*, where *z* is directed along the line $B\to A$, since we have a parallel-type transition. As origin of coordinates we take the point half-way between the nuclei. The latter are considered to be held fixed during our calculation at any desired distance *r* apart. The nuclei *B* and *A* are now respectively located at the points (0, 0, $-r/2$) and (0, 0, $r/2$). Eq. (5) then gives the exceedingly simple result

$$Q\approx r/2(1-S^2)^{\frac{1}{2}}. \qquad (6)$$

Very striking is the proportionality of the *effective dipole moment amplitude* $2eQ$ of the transition to *r*. This proportionality to *r* is a *characteristic feature* of the class of transitions here discussed. Its occurrence is obviously con-

[4] L. Pauling and E. Bright Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935), Chapter XII.

[5] Cf. R. S. Mulliken, J. Chem. Phys. **3**, 375 (1935).

[5a] R. S. Mulliken, J. Chem. Phys. **7**, 14 (1939).

TABLE I. *Calculated values of Q and f for N→E of* H_2^+.

r(A)	0	0.53	0.74	1.06(r_e)	1.58	2.11	∞
Q(A) from (6)	0.46	0.51	0.56	0.66	0.84	1.08	∞
Q(A) from (6a)	0	0.26	0.37	0.53	0.79	1.06	∞
Exact Q(A)	0.196						∞
f from (7)	0.75	0.57	0.55	0.47	0.33	0.25	0
f from (7a)	0	0.15	0.24	0.31	0.29	0.24	0
Exact f	0.139						0

nected with the fact that in our wave functions Eqs. (1) or (3) we have an electron which may go back and forth between nuclei A and B, the amplitude of such an oscillation being $r/2$, in rough agreement with two times Q of Eq. (6). Further, the frequency of the spectroscopic transition $N\rightarrow E$ is just equal, according to quantum mechanics, to the frequency of oscillation of the electron between nuclei A and B for a wave function formed by linear combination from those of N and E including the time factors.

The factor $1/(1-S^2)^{\frac{1}{2}}$ in Eq. (6), which becomes important at small r, may be taken as a symptom of the fact that Eqs. (1), (3), (6) are only approximate, and that the approximation gets worse as r decreases. The factor $1/(1-S^2)^{\frac{1}{2}}$ can be shown[6] to approach $a_0/3^{\frac{1}{2}}r$ as r approaches zero, so that Eq. (6) gives a finite value at $r=0$. This is considerably larger than the correct value (cf. Table I), which is easily calculated if we note that $\sigma_g 1s\rightarrow\sigma_u 1s$ of H_2^+ becomes $1s\rightarrow 2p\sigma$ of He^+ for $r=0$. For the latter we have $Q=\int(1s)_{He^+}z(2p\sigma)_{He^+}dv=0.196\times10^{-8}$ cm. On the whole, Eq. (6) would, empirically, probably be somewhat improved for small r values by dropping the factor $1/(1-S^2)^{\frac{1}{2}}$, leaving

$$Q\approx r/2. \qquad (6a)$$

However, Eq. (6a) has the opposite fault to Eq. (6) in giving too small values at small r (cf. Table I).

Table I includes values of Q calculated from Eqs. (6) and (6a), together with exact values for $r=0$ and $r=\infty$. The Eq. (6) values for $r=2.11$A and 1.58A are probably nearly correct, while that for the equilibrium value $r=r_e$ (1.06A) is probably at least roughly correct.

[6] $S=\int(1s_A)(1s_B)dv=(1+\alpha+\alpha^2/3)e^{-\alpha}$, with $\alpha=Z_{ef}r/a_0$, where $Z_{ef}=1$ for the H atom; first given by Heitler and London; a_0=Bohr radius of one-quantum orbit in H atom. For H^-, $Z_{ef}=0.725$.

Having Q, the absorption probability coefficient $B^N{}_E$ can be obtained using Eq. (I, 6). More instructive in some ways is the oscillator-strength $f^N{}_E$, since we know that the f's obey the sum rule $\sum_X f^N{}_X=1$ (in general, $\sum f^N{}_X=$ total number of electrons in the molecule). To calculate f, we can use Eq. (I, 9), with $D=Q^2$ taken from Eq. (3) or Table I; $G'=1$ in the present case. Thus we get, in the Eq. (3) approximation,

$$f^N{}_E\approx(2.74\times10^{10})\nu r^2/(1-S^2). \qquad (7)$$

Corresponding to Eq. (6a) for Q we have

$$f^N{}_E\approx(2.74\times10^{10})\nu r^2. \qquad (7a)$$

For the necessary ν values needed in Eq. (6), we may refer to calculations of Teller.[7] Table I contains f values calculated from Eqs. (7) and (7a).

From Table I it appears that f passes through a maximum as r increases. It is seen also that f is strikingly large for r values in the neighborhood of r_e. The calculated f values indicate that about 0.4 of the whole intensity of the entire absorption spectrum of H_2^+ is concentrated in the one transition $N\rightarrow E$. Unfortunately we have no experimental data on this transition, nor does there seem to be much prospect of getting any.

For $r=\infty$, in spite of $Q=\infty$, we have $f=0$, because ν approaches zero exponentially as r increases. As r approaches zero, the value of f becomes identical with that for the transition $1s\rightarrow 2p\sigma$ in He^+ (which is the same as f for $1s\rightarrow 2p\sigma$ in H); this value is just $\frac{1}{3}$ the total value for $1s\rightarrow 2p$, since the latter comprises the three equally intense transitions $1s\rightarrow 2p_x$, $1s\rightarrow 2p_y$, and $1s\rightarrow 2p_z(2p_z\equiv 2p\sigma)$.

For small r values, the fact that f for $N\rightarrow E$ in H_2^+ is comparable with f values for strong Rydberg series lines is of course explained by the fact that $N\rightarrow E$ actually becomes (one component of) the strongest Rydberg series line of He^+. For larger r values, however, it is clear that the large Q values (proportional to r for large r) and large f values are unrelated to this, but are connected with the "resonance" of an electron between the two centers.

[7] Cf., e.g., R. S. Mulliken, Rev. Mod. Phys. **4**, 44, 46 (1932). For $r=1.06$A, $\nu\approx100{,}000$ cm^{-1} for $N\rightarrow E$ of H_2^+.

3. One-Electron-Resonance Spectra in Many-Electron Molecules

Transitions more or less closely analogous to $N \rightarrow E$ of H_2^+ can be predicted in many-electron molecules, and some examples are known experimentally. Next in simplicity to $N \rightarrow E$ of H_2^+ is a predicted transition between two similar states[4] of He_2^+. By MO's, N here is $(\sigma_g 1s)^2(\sigma_u 1s)$, $^2\Sigma^+_u$ and E is $(\sigma_g 1s)(\sigma_u 1s)^2$, $^2\Sigma^+_g$, so that the transition consists primarily of a jump of one electron from a $\sigma_g 1s$ to a $\sigma_u 1s$ MO, just as in $N \rightarrow E$ of H_2^+.

It might seem more appropriate to refer to $N \rightarrow E$ in He_2^+ as a three-electron-resonance spectrum (cf. Pauling's designation "three-electron bond" for the electron configuration in state N of He_2^+), since all three electrons are equally engaged. However, the resonance process connected with the spectrum is essentially a resonance of *one electron at a time*, and we shall call it a one-electron resonance spectrum. Examples which involve simultaneous resonance of two or more electrons (true two- or several-electron-resonance spectra) are discussed in Section 6.

Other cases similar to that of He_2^+ are known experimentally in the spectra of many-electron molecules. The ultraviolet $^2\Pi_u \rightarrow {}^2\Pi_g$ O_2^+ bands involve an MO transition $\pi_g 2p \rightarrow \pi_u 2p$ in emission. Very similar, although the molecule is not homopolar, are the $^2\Pi \rightarrow {}^2\Pi$ bands of NO ("β-bands"), known in absorption and emission. Both these examples involve a transition between a π bonding and a corresponding π antibonding MO, and should have a Q roughly equal to r.

One can predict, therefore, that these should be very intense transitions. Experimentally, qualitative data are available for the absorption spectrum of NO. Although these data tend to show that the NO β-bands are not very strong, further investigation will be required before anything conclusive can be said.

[*Added in proof.*] In the new edition of Gilman's *Organic Chemistry*, Pauling has already recognized the existence in certain dyes (e.g. Döbner's violet) of the type of intense spectra here called charge-resonance spectra, and has pointed out very briefly that the transition electric moment should be very large, giving deep color.[7a] Both charge-transfer and charge-resonance spectra giving strong color will be discussed in later papers of this series.

4. One-Electron-Transfer Spectrum in H_2

We come now to the important class of parallel-type transitions whose consideration started the present work. As prototype we may take the $N\,{}^1\Sigma^+_g \rightarrow V\,{}^1\Sigma^+_u$ transition in H_2.

It would be possible to calculate exact values for the strength of this transition, at least for one value of r, since James and Coolidge have obtained very nearly exact expressions for the wave function of $N\,{}^1\Sigma^+_g$ over a range of r values in the neighborhood of its r_e, and Present has determined a similar expression for state V at its r_e.[8] Since, however, r_e of state V is 1.28A, while r_e of state N is 0.74A, the exact calculation of f for $r=1.28$A would not be applicable to $N \rightarrow V$ in absorption, for which $r=0.74$A would be required. Anyway, we are now interested not so much in an exact calculation for H_2 as in arriving at general formulas based on approximations which we can use also in other molecules where no exact wave functions are available.

Two types of approximation will be used here, the one based on MO wave functions, the other on AO functions. The former approximation is best for small and the latter for large r values.

The MO wave functions are

$$\left.\begin{aligned} \Psi_N &\approx \sigma_g 1s(1)\sigma_g 1s(2), \\ \Psi_V &\approx [\sigma_g 1s(1)\sigma_u 1s(2) + \sigma_u 1s(1)\sigma_g 1s(2)]/2^{\frac{1}{2}}. \end{aligned}\right\} \quad (8)$$

A spin factor $[\alpha(1)\beta(2) - \alpha(2)\beta(1)]/2^{\frac{1}{2}}$ has been omitted from each Eq. (8), since, in any case, it would drop out later in the integration to obtain Q.

It should be noted that because of the mutual interaction of the two electrons, the MO's $\sigma_g 1s$ and $\sigma_u 1s$ in Eq. (8) are not quite the same as the like-designated orbitals of H_2^+. Moreover, Eqs. (8) would give only approximations (though perhaps fairly good ones) even if the best possible MO's were used, whereas for H_2^+ the accurate MO's $\sigma_g 1s$ and $\sigma_u 1s$ directly constitute accurate wave functions Ψ_N and Ψ_E.

[7a] H. Gilman, *Organic Chemistry*, Vol. II (1938), pp. 1888–9.

[8] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933); *ibid.* **3**, 129 (1935). R. D. Present, J. Chem. Phys. **3**, 122 (1935).

The effective dipole moment eQ for $N \rightarrow V$ in H_2 corresponds (cf. Eq. (I, 4)) to

$$Q = \int \Psi_N (z_1 + z_2) \Psi_V d\tau, \tag{9}$$

where z_1 and z_2 refer to the two electrons. The coordinate system for the electrons may best be chosen in the same way as for the single electron in H_2^+ (cf. Eq. (5)). Substituting from Eqs. (8) in Eqs. (9), and noting that $\sigma_g 1s$ and $\sigma_u 1s$ are mutually orthogonal and may be taken as normalized, we get

$$Q \approx 2^{\frac{1}{2}} \int (\sigma_g 1s) z (\sigma_u 1s) dv, \tag{10}$$

where the integration is now over the space of a single electron. If we knew the exact forms of the true MO's $\sigma_g 1s$ and $\sigma_u 1s$, Eq. (10) might give us a fairly good approximation to the exact Q.

If we do not wish to go to a good deal of trouble, however, we must be content to make an approximation within an approximation, by using the rough LCAO forms (cf. Section 2) for the MO's in Eq. (10). These are given by Eqs. (3), the same equations as for H_2^+. Substituting these in Eq. (10), we get

$$Q \approx r/2^{\frac{1}{2}}(1-S^2)^{\frac{1}{2}}. \tag{11}$$

Thus, except for multiplication by a factor $2^{\frac{1}{2}}$ in Eqs. (10), (11), the expression for Q is exactly the same as for H_2^+ (cf. Eq. (6)), in agreement with the fact that in terms of MO's the transition is a jump $\sigma_g 1s \rightarrow \sigma_u 1s$, the same here as there. This supports the idea that such transitions (i.e., bonding→antibonding MO's) always have characteristically high intensity.

The new factor $2^{\frac{1}{2}}$ for Q means a factor 2 for A, B, and f. Thus for $f^N{}_V$ of H_2 (cf. Eq. (7) for H_2^+):

$$f^N{}_V \approx (5.48 \times 10^{10}) \nu r^2/(1-S^2). \tag{12}$$

The new factor 2 is evidently connected with the fact that now in state N there are two $\sigma_g 1s$ electrons *either* of which can jump, whereas in H_2^+ there was only one.

The following simplifications of Eqs. (11), (12) may perhaps represent improvements according to the empirical reasoning used above in introducing Eqs. (6*a*), (7*a*):

$$Q \approx r/2^{\frac{1}{2}}, \tag{11a}$$

$$f^N{}_V \approx (5.48 \times 10^{10}) \nu r^2. \tag{12a}$$

We now examine the AO approximation. Here for state N we have the well-known Heitler-London expression, while for state V we have (at least roughly[2]) a structure corresponding to H^+H^- and H^-H^+ in equal proportions. The approximate wave functions (omitting the spin factor just as we did in Eqs. (8)) are then

$$\left.\begin{aligned} \Psi_N &\approx [1s_A(1)1s_B(2) \\ &\qquad + 1s_B(1)1s_A(2)]/2^{\frac{1}{2}}(1+S^2)^{\frac{1}{2}}, \\ \Psi_V &\approx [1s^x{}_A(1)1s^x{}_A(2) \\ &\qquad - 1s^x{}_B(1)1s^x{}_B(2)]/2^{\frac{1}{2}}(1-S^{x2})^{\frac{1}{2}}. \end{aligned}\right\} \tag{13}$$

Here $1s^x$ refers to a $1s$ AO of H^- ($Z_{eff} = 0.725$ instead of 1), and $S^x = \int 1s^x{}_A 1s^x{}_B dv$.

Putting Eqs. (13) in Eq. (9) and integrating, we get

$$Q \approx U[S^0 r - 2\int (1s_A) z (1s^x{}_B) dv] \\ /[(1+S^2)(1-S^{x2})]^{\frac{1}{2}}, \tag{14}$$

where

$$U = \int (1s)(1s^x) dv = 0.962,$$

$$S^0 = \int (1s_A)(1s^x{}_B) dv = \int (1s^x{}_A)(1s_B) dv.$$

As a useful rough approximation to Eq. (14),

$$Q \approx Sr. \tag{14a}$$

Corresponding to Eqs. (14), (14*a*), we have

$$f^N{}_V \approx (1.096 \times 10^{11}) \nu U^2 [S^0 r - 2\int 1s_A z 1s^x{}_B dv]^2 \\ /(1+S^2)(1-S^{x2}), \tag{15}$$

$$f^N{}_V \approx (1.096 \times 10^{11}) \nu S^2 r^2. \tag{15a}$$

Comparing the AO equation (14) or most simply (14*a*) with the MO equations (11), (11*a*), the outstanding difference is the new factor S, which goes to zero as $r \rightarrow \infty$, and so causes Q to do the same, whereas in Eqs. (11), (11*a*), $Q \rightarrow \infty$ as $r \rightarrow \infty$. Since the correct result is $Q \rightarrow 0$ as $r \rightarrow \infty$, only Eqs. (14), (14*a*) are acceptable for large r values. The present case is, in this respect, very different from that of H_2^+, where the MO approximation is exact for all r values and is approached asympotically as $r \rightarrow \infty$ by the AO approximation. In H_2^+, $Q \rightarrow \infty$ as $r \rightarrow \infty$ is correct, since the fact that $\nu \rightarrow 0$ as $r \rightarrow \infty$ permits $f \rightarrow 0$ as required.

For r values near the equilibrium value r_e, Eqs. (15), (15a) agree qualitatively with (12) or (12a) in predicting high intensity for $N \rightarrow V$. Quantitatively, however, both approximations may be expected to be rather poor at such r values.

For small r values, we must definitely reject Eqs. (14), (14a), (15), (15a), but may accept Eq. (10) as fairly accurate; Eqs. (11), (11a) constitute approximations to Eq. (10). Unfortunately the LCAO approximation used for the MO's of (10) in order to get (11) becomes rather bad for small r values. Thus Eq. (11) is expected to give poor results for small and worse for large r values.

Summing up, we expect Eqs. (14), (15) to be rather accurate at large r values, with Eqs. (14a), (15a) as simple approximations to them (increasingly close as r increases). For moderate r values near r_e, Eqs. (14), (15) or (14a), (15a), and Eqs. (11), (12), or perhaps better (11a), (12a) may be expected to be roughly, but only roughly, correct. Equations not mentioned for a given range of r values are to be rejected. Small r values much less than r_e have of course little practical interest.

Table II contains Q and f values calculated for various r values in order to check the foregoing conclusions,—as it does. The table also gives an approximate idea of the actual magnitudes of Q and f as functions of r. The "exact" values for $r=0$ are based on a theoretical calculation by Wheeler for the He atom. Wheeler estimates the error of his calculation of f as not in excess of 30 percent and probably much less.[9] Table II shows the expected failure of Eqs. (11), (12) at $r=0$ and at $r=\infty$, of Eqs. (14), (15) at $r=0$, and of Eqs. (11a), (12a) at $r=\infty$. It suggests empirically that the simplified Eqs. (14a), (15a) are not so bad as the original Eqs. (14)–(15) at small r values; at large r the two sets differ little, but the theoretical Eqs. (14), (15) should be the more exact.

A consideration of available experimental dispersion and absorption data on H_2 in connection with the calculated f's in Table II will be postponed. Suffice it to say here that the data (which are not very adequate) are compatible with the calculations. Discussion of the calculations of Mrowka on H_2 (I, reference 2) will also be postponed. Possible more accurate calculations have been discussed in the first paragraph of this section.

TABLE II. *Calculated values of Q and f for $N \rightarrow V$ of H_2.*[9–11]

r(A)	0	0.74 (r_e)	1.056	1.584	2.112	∞
Q(A) by Eq. (11)	0.65	0.79	0.93	1.19	1.53	∞
Q by Eq. (11a)	0	0.52	0.75	1.12	1.50	∞
Q by Eq. (14)	0.83	0.72	0.69	0.59	0.45	0
Q by Eq. (14a)	0	0.56	0.62	0.55	0.40	0
Exact Q	0.22					0
f by Eq. (12)	0.79	0.69	0.84	1.18	1.64	∞
f by Eq. (12a)	0	0.30	0.55	1.04	1.58	∞
f by Eq. (15)	1.29	0.55	0.46	0.29	0.14	0
f by Eq. (15a)	0	0.33	0.38	0.25	0.11	0
Exact f	0.09					0

5. One-Electron-Transfer Spectra in Other Molecules

Transitions analogous to $N \rightarrow V$ of H_2 can be identified in the spectra of a number of molecules, polyatomic as well as diatomic (N = primarily atomic, V primarily ionic, by AO's; transition of an electron from a bonding to a corresponding antibonding orbital, by MO's). Some diatomic examples have been mentioned in earlier papers.[2,3] In the present section several transitions of this type in homopolar molecules are rather briefly discussed.

A difference in most molecules as compared with H_2 is that the bonding electrons are commonly p instead of $1s$ electrons. A result of this is that the overlapping integrals S are smaller in other molecules than in H_2; this is especially true for the $p\pi$ electrons which occur in double and triple bonds. Smaller S values give a greater divergence between Eqs. (11a), (12a) and Eqs. (14a), (15a). In the following we shall make calculations by both sets of equations.

It should, however, always be borne in mind in the following discussion that the calculation of S

[9] For ν data, needed in calculation of f's, cf. reference 7. The "exact" value of f at $r=0$ is based on J. A. Wheeler's calculated $f=0.27$ for the transition $1s^2$, $^1S \rightarrow 1s2p$, ^1P in the He atom (Phys. Rev. **43**, 260, 1933). Our f is $\frac{1}{3}$ this, since it corresponds just to $1s^2 \rightarrow 1s\sigma 2p\sigma$.

[10] Although state V probably has in good approximation a structure H^+H^- for moderate r values, it is very probable that it actually goes into H^- ($1s$)+H ($2s\sigma$, $2p\sigma$) *on dissociation*,[2] as a result of interactions of potential energy curves; in this case a considerable f would exist for large r and for $r=\infty$. If, for instance, V went into H ($1s$) +H ($2p\sigma$), f would be 0.278 for $r=\infty$, i.e., *twice* the value for $1s \rightarrow 2p\sigma$ in an H atom, since at $r=\infty$ there are two absorbing H atoms. Similar things may also often be expected for large r for the V states of other molecules. However, this is rather irrelevant to our present purposes.

[11] In making the calculations, S and S^2 were calculated from the equation given in reference 6, with $Z_{ef}=1$ for S and 0.725 for S^2. For Eqs. (14), (15), the integrals $\int 1s_A z 1s^2_B d\tau$ and S^0 were also evaluated, after transforming to elliptic coordinates.

for Eqs. (14*a*), (15*a*) requires in practice a further approximation in addition to those already made. On the other hand, it is important to note also that no such further approximation is involved in Eqs. (11*a*), (12*a*). The extra approximation for Eqs. (14*a*), (15*a*) comes about because it is necessary in practice to use approximate expressions for the two atomic orbitals over whose product S is an integral. Existing simple approximations, for example those of Slater, can be conveniently used, but there is no guarantee that they give very good S values. Just as with energy calculations involving similar approximations, we must judge the success of the calculations largely by comparison with experiment. In this connection it is a comforting fact, however, that intensity calculations which may be in error even by a factor of two or three are far from valueless, since observed intensities of allowed transitions vary in magnitude over several powers of ten.

It is worth noting here that Eqs. (14*a*), (15*a*) differ less from (14), (15) for most molecules than they do for H_2. This is because in most molecules A_2 (for example, a halogen molecule like I_2), the mean effective nuclear charge Z_{eff} differs relatively much less for A and A^- than it does[6] for H and H^-.

Let us consider first the halogens (Cl_2, Br_2, etc.). Neglecting all but the two bonding electrons, the transition $N \rightarrow V$ by MO's is

$$\cdots(\sigma_g np)^2, {}^1\Sigma^+_g \rightarrow \cdots(\sigma_g np)(\sigma_u np), {}^1\Sigma^+_u. \quad (16)$$

It can be shown that the other electrons, which are in closed shells, have no effect on the Q and f equations, so that these are exactly the same as for H_2, in both MO and AO approximations. We now have, however, $np\sigma$ instead of $1s$ AO's and $\sigma_g np$ and $\sigma_u np$ instead of $\sigma_g 1s$ and $\sigma_u 1s$ MO's.

The D band-system of I_2 (near and below $\lambda 2000$) may be cited as the first example of the type $N \rightarrow V$ in halogen molecules.[1] It was a desire to explain the (indirectly deduced) high intensity of this system that led to the present work. The results of theoretical calculations, given in Table III, do now in fact indicate a very high f value for the system. Direct quantitative experimental data are lacking, but the bands, although individually not very intense, are very numerous, so that the total f value may well be large. [The large number of the bands is explained by the broad and flat but deep potential energy curve with large r_e, which goes with the ionic character of the V state.[2]]

The $N \rightarrow V$ bands of Br_2 have recently been found by W. C. Price (private communication); those of Cl_2 and F_2 are not yet known. Calculations for these, also for HI, which is nearly nonpolar, are given in Table III. It is of especial interest to note how the calculated Q and even the f values increase with r_e of the halogen molecule, illustrating the characteristic proportionality of Q to r in Eqs. (11*a*), (12*a*). The surprisingly large S values, computed for a later detailed paper on halogen and halide spectra, are also interesting, although one cannot be certain how reliable they are; they were calculated using Slater's approximate wave functions for the halogen p atomic orbitals.

The f values obtained for the halogens using LCAO MO's (Eq. 12*a*) are doubtless too large, since for I_2 the Eq. (12*a*) f value of 2.17 even exceeds the maximum theoretically possible value 2 for the sum of all transitions in which the $(\sigma_g 1s)^2$ shell is excited. It seems likely that the true values lie between the LCAO values and the AO values, or perhaps nearer the latter.

The molecule O_2 is particularly interesting because here there exist quantitative absorption intensity measurements by Ladenburg and Van Voorhis.[12] The existence of the Schumann-Runge bands of O_2 and their accompanying continuum (which contains most of the intensity) constitute the main reason why vacuum spectrographs are necessary in the Schumann region of the ultraviolet. These bands have been interpreted[13] by MO's as the parallel-type transition

$$N\cdots(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2, {}^3\Sigma^-_g \longleftrightarrow V\cdots(\sigma_g 2p)^2(\pi_u 2p)^3(\pi_g 2p)^3, {}^3\Sigma^-_u. \quad (17)$$

According to this, the transition is in absorption essentially a jump of a single electron from a bonding $\pi_u 2p$ MO to the corresponding antibonding orbital $\pi_g 2p$. It ought then to be of an $N \rightarrow V$ type; or, let us say, of an $N \rightarrow V_\pi$ type, since excitation of a π electron is here involved. The $N \rightarrow V$ transitions already considered above

[12] R. Ladenburg, C. C. Van Voorhis, and J. C. Boyce, Phys. Rev. **40**, 1018 (1932); *ibid.* **43**, 315 (1933).
[13] Cf. R. S. Mulliken, Rev. Mod. Phys. **4**, 51–6, 82 (1932).

TABLE III. *S, Q and f values for N→V transitions in several molecules.*

MOLECULE	TRANSITION: STATES	TRANSITION: MOLECULAR ORBITALS	r_e(A) OF N	$\nu_{max}\times10^{-5}$ FOR $N\rightarrow V$	S (FOR $r=r_e$ OF N)	Q(A) BY (11a)	Q(A) BY (14a)	$f^N{}_V$ BY (12a)	$f^N{}_V$ BY (15a)	EXPTL. f
HI	$^1\Sigma^+\rightarrow{}^1\Sigma^+$	$\sigma\rightarrow\sigma^*$	1.60	[Est. 0.78]	0.50	1.13	0.79	1.09	0.54	—
I_2	$^1\Sigma^+_g\rightarrow{}^1\Sigma^+_u$	$\sigma_g5p\rightarrow\sigma_u5p$	2.66	0.56	0.39	1.88	1.04	2.17	0.67	(D bands)
Br_2	$^1\Sigma^+_g\rightarrow{}^1\Sigma^+_u$	$\sigma_g4p\rightarrow\sigma_u4p$	2.28	0.64	0.35	1.61	0.79	1.82	0.44	(observed)
Cl_2	$^1\Sigma^+_g\rightarrow{}^1\Sigma^+_u$	$\sigma_g3p\rightarrow\sigma_u3p$	1.98	[Est. 0.72]	0.30	1.39	0.60	1.55	0.28	—
F_2	$^1\Sigma^+_g\rightarrow{}^1\Sigma^+_u$	$\sigma_g2p\rightarrow\sigma_u2p$	(1.45)	—	0.17	1.03	0.25	—	—	—
O_2	$^3\Sigma^-_g\rightarrow{}^3\Sigma^-_u$	$\pi_u2p\rightarrow\pi_g2p$	1.20	0.69	0.17	0.85	0.20	0.55	0.030	0.19
	$^3\Sigma^-_g\rightarrow{}^3\Sigma^-_u$	$\sigma_g2p\rightarrow\sigma_u2p$	1.20	[Est. 1.0]	0.32	0.85	0.38	0.55	0.16	—
C_2H_4	$^1A_{1g}\rightarrow{}^1B_{1u}$	$b_{3u}2p\rightarrow b_{2g}2p$	1.34	0.57	0.27	0.95	0.36	0.56	0.081	See text

may then be called $N\rightarrow V_\sigma$ transitions, since they involve excitation of σ electrons.

If the transition is of $N\rightarrow V$ type, the $^3\Sigma^-_u$ upper state wave function should in AO approximation be of O^+O^-, O^-O^+ character. At first this appears to contradict the fact that the $^3\Sigma^-_u$ state is known to dissociate into neutral oxygen atoms (one ^3P and one ^1D, as first shown by Herzberg). But if we assume interaction of a $^3\Sigma^-_u$ potential energy curve, coming down from $O^+(^4S)+O^-(^2P)$ and having a broad deep minimum at large r_e, with a repulsive $^3\Sigma^-_u$ curve going up from the $^3P+{}^1D$ asymptote, we have a satisfactory explanation of the observed facts.

The high intensity of the observed absorption supports this explanation, since AO calculations made by the writer indicate that the transition from N to a $^3\Sigma^-_u$ state having a pure $^3P+{}^1D$ wave function would have zero intensity. The dissociation behavior of the V_π $^3\Sigma^-_u$ of O_2 here is, as a matter of fact, similar to that of V states in general, including that of H_2.[10] While there are good reasons for believing that V state wave functions can be rather well approximated by A^+A^-, A^-A^+ structures for small r, they commonly go over, through progressive stages of mixing, into the wave functions of a pair of neutral atoms on dissociation.

The wave functions for the N and V_π states of O_2 are complicated, especially by AO's. However, on writing out the complete antisymmetrical wave functions for each of the two approximations, substituting in Eq. (I, 4), and integrating, exactly Eq. (11) and substantially Eq. (12) are found for Q, just the same as for $N\rightarrow V$ of H_2. [Details will be postponed to a later paper.] Hence Q and f can be calculated by the same equations as for the other molecules in Table III.

As expected for π bonding electrons,

$$S=\int(2p\pi_A)^*(2p\pi_B)dv$$

comes out to be rather small (0.17, cf. Table III, when Slater AO's are used; it seems possible that with more accurate AO's, the calculated S would be larger). As a result there is an unusually great discrepancy between the f values calculated by Eqs. (12a) and (15a), and the value from (15a) is unusually small for an $N\rightarrow V$ transition.

Section 6 below helps us to see why the AO approximation gives a much smaller f than the LCAO approximation. As is well known, LCAO wave functions can be constructed by taking suitable linear combinations of neutral and ionic AO wave functions; for example, ψ_N of H_2 in LCAO approximation is formed from a 50,50 linear combination of the AO functions for ψ_N and ψ_Z (cf. Eqs. (21) below for ψ_Z),—while ψ_V is of identical form in AO and LCAO approximations. Similarly, to get the LCAO ψ's in O_2, the $N\,^3\Sigma^-_g$ AO wave function must be admixed with some $Z\,^3\Sigma^-_g$ (from O^+O^-, O^-O^+, cf. (21) below) and with some $ZZ\,^3\Sigma^-_g$ (from $O^{++}O^=$, $O^=O^{++}$, cf. (26), (27) below). Also the wave function of state $V_\pi\,^3\Sigma^-_u$ of O_2, which is already of O^+O^-, O^-O^+ character by AO's, must have some $VV\,^3\Sigma^-_u$ ($O^{++}O^=$, $O^=O^{++}$, cf. (26), (27)) mixed into it. Now as will be shown in Section 6, AO transitions of the type $V\leftrightarrow Z$ and $VV\leftrightarrow ZZ$ are respectively two-electron-resonance and four-electron-resonance spectra, and have extremely large Q's ($Q\approx r$ and $Q\approx 2r$ respectively, cf. Eq. (22) and discussion in Section 6). From this it can be seen why ionic admixtures and so the LCAO approximation greatly increase Q and f values, as compared with the AO approximation using only neutral atoms for state N.

Comparing the observed value $f=0.193$ with the two discordant calculated values $f=0.030$ by Eq. (15a) and 0.55 by Eq. (12a), we find that it lies more or less midway between them. This is not unreasonable, since the true wave functions are believed to lie more or less between those given by the two approximations. The comparison between observed and calculated f values

for O_2 gives us valuable indications about what to expect in other cases.

Before finally accepting this conclusion, one must of course make sure that the observed continuum which follows the Schumann-Runge bands actually all (or nearly all) belongs to the same electron transition. A rather careful examination of other possibilities indicates that this condition really is fulfilled. Several transitions can be predicted which should fall in this region of the spectrum, but it is fairly sure, although not absolutely certain, that all are weak.

One strong transition from state N to a second V state, this time a V_σ state,

$$\cdots(\sigma_g 2p)(\pi_u 2p)^4(\pi_g 2p)^2(\sigma_u 2p),\ ^3\Sigma^-_u \qquad (18)$$

is predicted (cf. Table III), but its estimated position is at about λ1000, and it is practically out of the question that it can overlap our continuum with maximum at λ1450. Aside from this, transitions from state N to the two following states might possibly have considerable intensity:

$$\cdots(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)(\sigma_u 2p),\ ^3\Pi_u, \qquad (19)$$

$$\cdots(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)(3p\pi_u),\ ^3\Sigma^-_u. \qquad (20)$$

However, the transition from N to the $^3\Pi_u$ of (19) involves an MO transition $\pi_g 2p \rightarrow \sigma_u 2p$ which is well known in the spectra of the halogens (cf. later paper), and which there has an f value that never exceeds 0.004. It is hardly likely, then, that this transition makes an important contribution to the total intensity of our continuum. The transition from N to the $^3\Sigma^-_u$ of (20), although it is a Rydberg series transition, also probably has too small an f value to be important here, according to rough estimates of the integrals involved in the appropriate expression for Q.

It should be mentioned that the experimental absorption curve[12] shows evidence of a small shoulder on its long wave-length side. This may well belong to one of the transitions just discussed, perhaps to the $N \rightarrow {}^3\Pi_u$. However, the shoulder corresponds to only a minor fraction of the total f value.

In polyatomic molecules having electronic structures related to those of diatomic molecules, it is possible to identify certain transitions as belonging to the type $N \rightarrow V$. In the molecules H_2O_2, N_2H_4, C_2H_6, CH_3NH_2, etc., which are rather closely analogous to the halogens, $N \rightarrow V_\sigma$ undoubtedly falls in the vacuum spectrograph region just as it does for the latter. Analogous to O_2 are C_2H_4 and B_2H_6, also N_2H_2, which, however, is known only in derivatives (azobenzene, etc.). Analogous to N_2 is C_2H_2.

As an example, let us consider C_2H_4. According to earlier work of the writer,[14] the normal and first excited states may be described as

$$N{:}\cdots(a_{1g}2p)^2(b_{3u}2p)^2,\ ^1A_{1g}, \qquad (21)$$

$$T,\ V{:}\cdots(a_{1g}2p)^2(b_{3u}2p)(b_{2g}2p),\ ^{3,1}B_{1u}. \qquad (22)$$

The $a_{1g}2p$ MO (called $[\sigma+\sigma,\ a_{1g}]$ in an earlier (1935) paper) is analogous to the $\sigma_g 2p$ bonding orbital in O_2 (cf. (17)), the pair of electrons in this orbital constituting the first bond of the double bond. The $b_{3u}2p$ MO (called $[x+x,\ b_{3u}]$ previously) is analogous to the $\pi_u 2p$ bonding orbital in O_2, the $(b_{3u}2p)^2$ pair constituting the second bond of the double bond and giving the latter its characteristic properties. The excited orbital $b_{2g}2p$ in (22),—called $[x-x,\ b_{2g}]$ previously,—is analogous to the antibonding orbital $\pi_g 2p$ in O_2. The transition from $^1A_{1g}$ of (21) to $^1B_{1u}$ of (22) involves a jump of one electron from a bonding to the corresponding antibonding MO, and so, as far as MO's are concerned, fulfills the definitional requirements for an $N \rightarrow V$ transition. Also in terms of AO's, it has the usual characteristics, the $^1B_{1u}$ state having a structure $(CH_2^+)(CH_2^-)$, as was pointed out in the writer's 1932 paper. The transition is thus of the same type as $N \rightarrow V_\pi$ in O_2.

In O_2, the MO's $\pi_u 2p$ and $\pi_g 2p$ each have twofold degeneracy. In C_2H_4 this degeneracy is broken up because of the altered symmetry; two of the resulting MO's, corresponding to one component of $\pi_u 2p$ and one of $\pi_g 2p$,—and called $[y+y]$ and $[y-y]$ in 1935,—are used in the C−H bonds. The $b_{3u}2p$ and $b_{2g}2p$ orbitals in (21) and (22) respectively correspond to the second component of $\pi_u 2p$ and of $\pi_g 2p$ of O_2. Thus the MO transition $b_{3u}2p \rightarrow b_{2g}2p$ in C_2H_4 which occurs for (21)→(22) is entirely analogous to the $\pi_u 2p \rightarrow \pi_g 2p$ transition (17) in O_2.

The results of calculations similar to those for $N \rightarrow V_\pi$ of O_2 are given in Table III. The calculated f value is about the same as for O_2 (somewhat larger in the AO approximation, because of relatively tighter bonding). Experimentally, there exists for a number of C_2H_4 derivatives and without much doubt for C_2H_4 itself, a broad spectrum with ν_{max} at about 57,000, which can be identified without much question as $N \rightarrow V$.[14, 15] There seem, however, to be no reliable intensity data for the transition; but what data there are appear compatible with what one might expect according to Table III and the experience with O_2 discussed above. Quantitative measurements

[14] R. S. Mulliken, Phys. Rev. **41**, 75 (1932); *ibid.* **43**, 297 (1933); J. Chem. Phys. **3**, 522 (1935).

[15] E. P. Carr and H. Stücklen, J. Chem. Phys. **4**, 760 (1936). Also Snow and Alsopp, reference 16.

would be very desirable in order that we might make a comparison with the two theoretical values as we did for O_2.

Several investigations[16] agree in indicating that a series of bands, plus apparently continuous background, begin at λ2000 in C_2H_4 and go with increasing intensity toward shorter wave-lengths. The maximum of intensity, marked by a band, appears to be at $\nu = 56{,}960$ according to a figure of Scheibe and Grieneisen.[16] [To be sure, they state that they do not feel certain that these bands really belong to C_2H_4; but other available evidence, including that on C_2H_4 derivatives, tends in the writer's opinion to remove this doubt.] Since their figure is based only on appearance pressures, it does not give any very certain evidence as to the intensity of the absorption. However, if the relation between appearance pressure and absorption coefficient is about the same as for a number of other molecules discussed in a preceding paper by Scheibe, Povenz, and Linström,[17] one can arrive at an estimate of $f \approx 0.1$ or 0.2 for the broad absorption region beginning near $\nu = 50{,}000$ and having its maximum perhaps near $\nu = 57{,}000$. On the other hand, estimates of absorption coefficients based directly on the appearance pressures given in Scheibe and Grieneisen's paper, assuming that a band "appears" when the absorption is 10 percent, lead to very small f values ($f \approx 0.0004$). But, on the other hand, Scheibe, Povenz, and Linström report for an absorption region of trimethylethylene which is clearly $N \rightarrow V$ for that molecule, absorption coefficients so large that, in connection with data of Carr and Stücklen,[15] they indicate $f > 4$ for this electronic transition, which is impossibly large. On the whole, it would seem that the existing data are untrustworthy.

The $N \rightarrow V$ transition in C_2H_4 is overlapped (cf. Scheibe and Grieneisen[16]) by another transition beginning with an intense band at $\nu = 57{,}320$. This has been shown by Price[16] to be in all probability the first member of a Rydberg series. It is pretty clear from the intensity distribution that we have to deal here with a new transition. The $N \rightarrow V$ spectrum rises gradually to a broad maximum of intensity (more clearly seen in the C_2H_4 derivatives[15, 16]), while the Rydberg series transition starts suddenly with high intensity and covers a much more moderate frequency range.

The $N \rightarrow V$ transition gets broader and broader as radicals are substituted for H atoms in C_2H_4. This has been shown in figures by Carr and Stücklen, who emphasize that the long wave-length *beginning* of the $N \rightarrow V$ absorption is shifted progressively toward longer wave-lengths as H atoms are successively substituted. Their figures show, however, that the position of maximum intensity remains nearly constant near $\nu = 57{,}000$ in most derivatives. Hence it is seen that substitution *broadens* the spectrum. By way of explanation, one may postulate that the restoring force constant for torsional vibration gets smaller as a result of substitution. That this will account for the broadening of the spectrum can be seen from a study of figures in the writer's 1932 paper.[14] The general appearance of these spectra (mostly bands apparently superposed on a continuum) can also be understood from these figures. The figures indicate that all or part of the spectrum may be composed of fine discrete bands and lines, but so closely packed as to appear continuous at low dispersion.

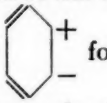
In benzene (C_6H_6) we have an example of another type of polyatomic molecule, with double bonds like C_2H_4 but containing three of them, altered too by the phenomenon of resonance. In spite of resulting complications, one can predict an electronic transition which can fairly be labeled $N \rightarrow V$.

In a recent paper Sklar has discussed the spectrum of benzene.[18] He concludes that, aside from several weak transitions at longer wave-lengths forbidden by electronic selection rules, the longest wave-length allowed transition is one of the type ${}^1A_{1g} \rightarrow {}^1E_{1u}$, giving a series of bands near λ2000. Using AO wave functions, Sklar calculates approximately the relative energies of the two states, hence the frequency of the transition. It is interesting to observe that Sklar

[16] J. Stark, et al., Jahrb. der Rad. und Elek. **10**, 10–188 (1913); Int. Crit. Tables, Vol. 5; G. Scheibe and H. Grieneisen, Zeits. f. physik. Chemie **25B**, 54 (1934); C. P. Snow and C. B. Alsopp, Trans. Faraday Soc. **30**, 93 (1934); W. C. Price, Phys. Rev. **47**, 451 (1935).

[17] G. Scheibe, F. Povenz, and C. F. Linström, Zeits. f. physik. Chemie **20B**, 283 (1933).

[18] A. L. Sklar, J. Chem. Phys. **5**, 669 (1937); M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938).

had to use wave functions of ionic character such as  for the $^1E_{1u}$ state. The normal state is homopolar in AO approximation. We now find that the transition has precisely the characteristics of our $N \rightarrow V$ type. [To be sure, the transition is a perpendicular-type instead of a parallel-type one with reference to the chief axis of symmetry, but this difference as compared with molecules considered above is only superficial from the point of view of the intensity theory.] Calculations to be reported in IV of this series show that the f value for the transition ought to be three or four times as large as for C_2H_4, corresponding to the three double bonds.

Experimentally, intensity data of Henri on several of the longest wave-length bands of the transition indicate an experimental f value of about 0.1.[19] Referring, however, to a figure by Carr and Stücklen which shows a series of bands from about λ2060 to λ1860, then a considerably more intense broad region of absorption with maximum at about λ1800, the total f may well be much larger. That the second region is the more intense is confirmed by Price's description; Price,[16] using very low pressure, observed only "a strong continuous absorption starting fairly sharply around 1840A," and fading out to 1600A.

The fact that the absorption region appears to consist of two overlapping parts (cf. Carr and Stücklen's figure) need not necessarily contradict the identification of the whole with $^1A_{1g} \rightarrow {}^1E_{1u}$, for two reasons: (*a*) Carr and Stücklen's figure may perhaps be somewhat deceptive, since it is not based on quantitative data; (*b*) the equilibrium symmetry of the molecule should be altered in the upper state, causing the degenerate state $^1E_{1u}$ to split into two nondegenerate states, according to the theorem of Jahn and Teller (I, reference 9); although this would not (because of the Franck-Condon principle) lead to a pronounced subdivision of the spectrum into two parts, it might account for the rather slight observed subdivision.

Possibly the second region consists in part of a Rydberg series transition. This is suggested by a number of superposed fine bands indicated in Carr and Stücklen's figure, also by the analogous case of C_2H_4 discussed above. However, the general character of the absorption region agrees with that for a bonding→antibonding transition, and indicates that it is predominantly not of Rydberg series type.

A fuller discussion of systems containing resonating and conjugated double bonds is planned for the next paper of this series.

[19] N. Q. Chako, J. Chem. Phys. **2**, 648 (1934).

6. Multiple-Resonance and Multiple-Transfer Spectra

In Sections 2, 3, we have considered one-electron-resonance spectra and in Sections 4, 5, one-electron-transfer spectra. It will now be shown that, even in diatomic molecules, resonance or transfer spectra involving two or more electrons simultaneously can have high intensity, at least according to the AO approximation. In the same approximation, two- or several-electron jumps have zero intensity in atomic spectra.

As the simplest example (though not likely to be observed experimentally) of a two-electron-resonance spectrum, consider the transition between the states[2] V and Z in the H_2 molecule. State Z is a $^1\Sigma^+_g$ state with MO electron configuration $(\sigma_u 1s)^2$, while V is $(\sigma_g 1s)(\sigma_u 1s)$, $^1\Sigma^+_u$. Omitting the spin factor,

$$\begin{aligned}\Psi_V &\approx [\sigma_g 1s(1)\sigma_u 1s(2)+\sigma_u 1s(1)\sigma_g 1s(2)]/2^{\frac{1}{2}},\\ \Psi_Z &\approx \sigma_u 1s(1)\sigma_u 1s(2).\end{aligned} \tag{23}$$

The calculation of Q for $V \leftrightarrow Z$ by LCAO MO's is very similar to that for $N \rightarrow V$ (cf. Eqs. (8) *et seq.*) and leads to the identical result (cf. Eq. (11)):

$$Q_{V \rightarrow Z} \approx r/2^{\frac{1}{2}}(1-S^2)^{\frac{1}{2}}. \tag{24}$$

Using AO's, states V and Z can both be approximated by an ionic structure H^+H^-, H^-H^+, so that in this approximation $V \leftrightarrow Z$ is very different from $N \leftrightarrow V$; omitting the spin factor,

$$\left.\begin{aligned}\Psi_V &\approx [1s^x{}_A(1)1s^x{}_A(2)\\ &\qquad -1s^x{}_B(1)1s^x{}_B(2)]/2^{\frac{1}{2}}(1-S^{x2})^{\frac{1}{2}},\\ \Psi_Z &\approx [1s^x{}_A(1)1s^x{}_A(2)\\ &\qquad +1s^x{}_B(1)1s^x{}_B(2)]/2^{\frac{1}{2}}(1+S^{x2})^{\frac{1}{2}}.\end{aligned}\right\} \tag{25}$$

Putting Eqs. (25) into the proper expression $Q=\int \Psi_V(z_1+z_2)\Psi_Z d\tau$, we get, on integrating,

$$Q=r/(1-S^{x4})^{\frac{1}{2}}. \tag{26}$$

The transition $V \rightarrow Z$ by AO's is of exactly the same character as $N \rightarrow E$ in H_2^+, except that here *two* electrons (simultaneously) can go back and forth ("resonate") between nuclei A and B, while in H_2^+ only one goes back and forth (compare Eqs. (25) with Eqs. (1), and see the discussion following Eq. (6)). Eq. (26) is essentially the same as Eq. (6), or (6*a*), except for a multiplying factor two corresponding to the two-electron-resonance in the present case. In the transition $V \rightarrow Z$, it is as if the *two* electrons oscillated *in phase* each with an amplitude r and frequency $(E_Z - E_V)/h$. Because they oscillate in phase, all quantities measuring *intensity* (A, B, f, etc.) are multiplied by a factor $2^2 = 4$, as compared with the one-electron-resonance in H_2^+. These results are interesting in indicating the possibility of intense molecular spectra involving two- or several-electron resonance (cf. Section 5, p. 26 for some further conclusions). These transitions have no counterpart in the spectra of atoms.

Various types of several-electron-resonance spectra can easily be described for diatomic molecules. These can be indicated by giving suitable pairs of wave functions. Using symbols ϕ, χ, to indicate various different AO's, we can readily specify several such types, for example (omitting spin and normalization factors)

$$\Psi_N,\ \Psi_E \approx [\phi_A(1) \pm \phi_B(2)], \tag{1}$$

$$\Psi_V,\ \Psi_Z \approx [\phi_A(1)\phi_A(2) \mp \phi_B(1)\phi_B(2)], \tag{25}$$

$$\Psi_X,\ \Psi_Y \approx [\phi_A(1)\phi_A(2)\chi_A(3) \pm \phi_B(1)\phi_B(2)\chi_B(3)], \tag{27}$$

$$\Psi_M,\ \Psi_N \approx [\phi_A(1)\phi_A(2)\chi_B(3) \pm \phi_B(1)\phi_B(2)\chi_A(3)], \tag{28}$$

$$\Psi_{\mathrm{I}},\ \Psi_{\mathrm{II}} \approx [\{\phi_A(1)\chi_B(2) + \chi_A(1)\phi_B(2)\} \pm \{\phi_B(1)\chi_A(2) + \chi_B(1)\phi_A(2)\}], \tag{29}$$

$$\Psi_{VV},\ \Psi_{ZZ} \approx [\phi_A(1)\phi_A(2)\chi_A(3)\chi_A(4) \pm \phi_B(1)\phi_B(2)\chi_B(3)\chi_B(4)]. \tag{30}$$

[If there are more than two electrons, as in Eqs. (27), (28), (30), each of the two terms in each Ψ ought first to be multiplied by appropriate spin functions and then made antisymmetrical in the electrons; but the correct behavior for our purposes is indicated by the primitive forms given above.]

The transitions $\Psi_N \rightarrow \Psi_Z$ and $\Psi_{\mathrm{I}} \rightarrow \Psi_{\mathrm{II}}$ represent two kinds of two-electron-resonance spectra, $\Psi_X \rightarrow \Psi_Y$ and $\Psi_M \rightarrow \Psi_N$ two kinds of three-electron-resonance spectra, and $\Psi_{VV} \rightarrow \Psi_{ZZ}$ a four-electron-resonance spectrum. In $\Psi_N \rightarrow \Psi_A$, $\Psi_N \rightarrow \Psi_Z$, $\Psi_X \rightarrow \Psi_Y$, and $\Psi_{VV} \rightarrow \Psi_{ZZ}$, the respectively one, two, three, and four electrons resonate in phase, and Q is respectively equal approximately to $r/2$, $2r/2$, $3r/2$, and $4r/2$. An example of $\Psi_X \rightarrow \Psi_V$ could be based on $[\mathrm{Be}^-(s^2p\sigma) \cdot \mathrm{Be}^{++}]$; of $\Psi_M \rightarrow \Psi_N$ on $[\mathrm{Be}(s^2) \cdot \mathrm{Be}^+(p\sigma)]$. In $\Psi_M \rightarrow \Psi_N$, two electrons move in phase, the third in opposite phase, and Q comes out approximately $r/2$ just as for one-electron resonance. In $\Psi_{\mathrm{I}} \rightarrow \Psi_{\mathrm{II}}$ (example, $[\mathrm{H}(1s) \cdot \mathrm{H}(2p\pi)]$, $^1\Pi_u \rightarrow {}^1\Pi_g$), we find Q to be precisely zero in our approximation, corresponding to the fact that the two electrons resonate in opposite phase. [The LCAO approximation, however, predicts a high intensity for $\Psi_{\mathrm{I}} \rightarrow \Psi_{\mathrm{II}}$. This is probably correct, since it can be shown that the AO approximation is very poor in this case. These facts, however, do not affect the principle illustrated by the example.]

Examples of several-electron-resonance spectra in diatomic molecules could be multiplied, and in polyatomic molecules innumerable types could be set up, but the foregoing suffices to show what is involved. For the case where electrons on just one pair of equivalent atoms A and B are concerned, our conclusion is the following. By AO's, Q for a transition between a symmetrical state (say $\Psi_\alpha + \Psi_\beta$) and the corresponding antisymmetrical state (say $\Psi_\alpha - \Psi_\beta$), —or vice versa,—is proportional to the A, B internuclear distance r, and to the *net* number of electrons which go from A to B (or B to A) when we go from wave function Ψ_α to Ψ_β. In applying this in practise, we must of course first ask ourselves how good the AO approximation is, and in any case it is advisable also to examine the LCAO MO approximation,—and further, to consider how well the true MO's are approximated by LCAO forms.

Sometimes the LCAO MO gives the same result as the AO approximation, but sometimes a larger, sometimes a smaller result. As an example, consider the three transitions $N \rightarrow E$ in H_2^+, $N \rightarrow V$ in H_2, and $V \rightarrow Z$ in H_2. By AO's, we have for Q in the three cases respectively $r/2(1-S^2)^{\frac{1}{2}}$, $r/2^{\frac{1}{2}}(1-S^2)^{\frac{1}{2}}$, $r/2^{\frac{1}{2}}(1-S^2)^{\frac{1}{2}}$. In the

three cases the LCAO value of Q is respectively the same as, larger than, and smaller than, the AO value.

A few examples of parallel-type several-electron-transfer spectra will now be indicated. Molecules like O_2 should show, in their vacuum-region absorption spectra, two-electron-transfer transitions from state N to some states V whose AO wave functions can be briefly indicated by configuration symbols as follows:

$$\left.\begin{aligned}
&\Psi_N \approx (2p\sigma_A \cdot 2p\sigma_B)(2p\pi_A)^3 \cdot (2p\pi_B)^3,\ {}^3\Sigma^-_g,\\
&\Psi_{VV} \approx [(2p\sigma_A{}^2 2p\pi_A{}^4)2p\pi_B{}^2\\
&\qquad\qquad -(2p\sigma_B{}^2 2p\pi_B{}^4)2p\pi_A{}^2], {}^3\Sigma^-_u,\\
&\Psi_{VV'} \approx [(2p\sigma_A{}^2 2p\pi_A{}^4)2p\pi_B{}^2\\
&\qquad\qquad -(2p\sigma_B{}^2 2p\pi_B{}^2)2p\pi_A{}^4], {}^3\Sigma^-_u.
\end{aligned}\right\} (31)$$

Here Ψ_N is the ordinary normal state of O_2, built according to AO's from two normal O atoms each with the configuration $1s^2 2s^2 2p\sigma 2p\pi^3$, $2p\sigma_A$ forming an ordinary pair bond with $2p\sigma_B$, and the two $2p\pi^3$ groups giving a second bond. State VV has structure $O^{++}O^{=}$, $O^{=}O^{++}$, with configuration $2p\pi^2$ and state ${}^3P\Sigma^-$ for O^{++}, and $2p^6$, ${}^1S$ for $O^{=}$. Omitting the four nonresonating electrons, i.e., the two $2p\pi_A$ and two $2p\pi_B$ electrons which are common to the two terms in Ψ_{VV} of Eq. (31), this Ψ_{VV} is seen to be of the type indicated in Eq. (30). State VV' has a structure composed of two neutral O atoms, one with configuration $2p\sigma^2 2p\pi^2$ and state ${}^3P\Sigma^-$, the other with configuration $2p\pi^4$ and state ${}^1D\Sigma^+$ or ${}^1S\Sigma^+$. [With molecular quantization of the p electrons (σ, π), single definite atomic states (S, P, D) cannot always be specified to correspond.]

The transition $\Psi_N \rightarrow \Psi_{VV}$ involves simultaneous transfer of one σ and one π electron from atom A to atom B or vice versa. $\Psi_N \rightarrow \Psi_{VV'}$ involves a simultaneous transfer from A to B of one σ and from B to A of one π electron; or vice versa; the net number of electrons transferred is zero.

An example of a parallel-type three-electron-transfer spectrum can be predicted in the transition between the following possible states Ψ_N, Ψ_{VVV} of N_2 (using AO's):

$$\left.\begin{aligned}
&\Psi_N \approx (2p\sigma_A \cdot 2p\sigma_B)(2p\pi_A{}^2 : 2p\pi_B{}^2),\ {}^1\Sigma^+_g,\\
&\Psi_{VVV} \approx [(2p\sigma_A{}^2 2p\pi_B{}^4) - (2p\sigma_B{}^2 2p\pi_A{}^4)],\ {}^1\Sigma^+_u.
\end{aligned}\right\} (32)$$

State VVV here corresponds to a structure N^+N^-, N^-N^+ with configuration $2p\sigma^2$ on N^+ and $2p\pi^4$ on N^-. The transition $\Psi_N \rightarrow \Psi_{VVV}$ involves simultaneous transfer of one σ electron from B to A and two π electrons from A to B, or vice versa; the net number of electrons transferred is one.

When the Q's are calculated for the above examples, using properly antisymmetrical wave functions, the results (to an approximation similar to that used in Eq. (14a)) appear to be as follows:[20]

$$\left.\begin{aligned}
&N \rightarrow VV \text{ of (31)}, \quad Q \approx 2{}^1S_\sigma S_\pi{}^2 r,\\
&N \rightarrow VV' \text{ of (31)}, \quad Q \approx 0,\\
&N \rightarrow VVV \text{ of (32)}, \quad Q \approx 2S_\sigma S_\pi{}^2 r.
\end{aligned}\right\} (33)$$

It is found that Q^2 is proportional to the *net* number of electrons transferred ($1+1=2$ in $N \rightarrow VV$, $1-1=0$ in $N \rightarrow VV'$, and $2-1=1$ in $N \rightarrow VVV$). Q also includes a factor S for each electron transferred ($S_\sigma = \int (2p\sigma_A)(2p\sigma_B)dv$, $S_\pi = \int (2p\pi_A{}^*)(2p\pi_B)dv$).

The outstanding fact is that simultaneous jumps of more than one electron can occur with considerable intensity provided there is a net jumping of charge from one atom to another. However, because of the S factors, jumps of more than two electrons are not very likely (cf. Table III for some S values). Further, such multiple-electron-transfer spectra may be expected to fall in the region of high frequencies, and their upper energy levels to be mixed up with various others, so that such spectra are more of theoretical interest than of practical importance. The same may be said of multiple-resonance spectra.

The foregoing discussion of multiple-transfer spectra has been based on AO's. Because of the high energies and probable mixing-up of the upper energy levels involved, it is probably rather meaningless to try to set up a one-to-one correspondence between a definite AO approximation and a definite MO approximation for some supposed actual energy level. However, let us consider state VV of Eq. (33). The most nearly corresponding MO state seems to be

$$VV: \quad \cdots(\pi_u 2p)^3(\pi_g 2p)^3(\sigma_u 2p)^2,\ {}^3\Sigma^-_u. \quad (34)$$

The configuration for state N of O_2 is given in

[20] These have not been checked carefully. Possibly there may be errors in the numerical factors.

(17). According to (17) and (34), the transition $N \rightarrow VV$ involves a three-electron jump in terms of MO's (two $\sigma_g 2p$ and one $\pi_u 2p$ electrons must make a change). Since in the pure-electron-configuration MO approximation for molecules (just as in the pure-electron-configuration AO approximation for atoms), only one-electron jumps are permitted, we have here most emphatically $Q=0$ for $N \rightarrow VV$. This difference between the results of the two approximations indicates that the actual transition identifiable as $N \rightarrow VV$ is weaker than Eqs. (33) indicate. Perhaps a considerable part of the intensity predicted by (33) for $N \rightarrow VV$ in O_2 is transferred to the two $N \rightarrow V$ transitions of Section 6 (cf. discussion on p. 31).

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The Further Concentration of N^{15}*

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A further study has been made on the application of the chemical exchange reaction between ammonia gas and ammonium nitrate in water to the problem of securing high concentrations of the nitrogen isotope of atomic weight 15. The apparatus consists of several glass packed columns filled with efficient packing materials arranged in cascade, such that a smaller second column operates on the product from the first and a third column operates on the product from the second. With this arrangement of columns we have secured 72.8 percent N^{15} and have produced sufficient quantities of concentrated material to investigate many of the physical properties of N^{15} and its compounds.

THE concentration of N^{15} by a chemical exchange reaction has been described by Urey, Huffman, Thode, and Fox.[1] The method depends on the isotopic exchange between ammonia gas and an ammonium salt solution, according to the equation

$$N^{15}H_3(g) + N^{14}H_4^+(\text{Sol.}) \rightleftarrows N^{14}H_3(g) + N^{15}H_4^+(\text{Sol.}),$$

for which the equilibrium constant is about 1.023. The theory of the method is essentially that of a distillation in which a counter current flow of liquid and gas is maintained in apparatus of the distillation column type. However, the gaseous phase in this chemical exchange process is ammonia gas, and the liquid phase an ammonium salt in water. The process consists of a flow of the liquid phase downward through a fractionating column, the liberation of the ammonia by the addition of sodium hydroxide and subsequent boiling, and the return of the ammonia upward through the column. In operation N^{15} is transported down the column since it concentrates in the liquid phase, and when a steady state has been reached, under conditions of total reflux at the bottom and with an infinite reservoir of material at the top, there will be an exponential distribution of N^{15} in the working material through the column.

By this method these authors produced a $6\frac{1}{2}$-fold change in the concentration, or 2.5 percent N^{15}, using ammonium sulphate in a single fractionating column. The advantage of the method is that it is capable of a very much larger transport than those previously used. In their experiments the transport was approximately 100 times that of the Hertz cascade diffusion method, and they produced substantial amounts of N^{15} of sufficiently increased concentrations for many experiments. With the modified apparatus described in this paper the transport has been further increased by a factor of about ten.

The increased concentrations obtained with the single column were not sufficiently high to enable one to investigate the physical properties

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[1] J. Chem. Phys. 5, 856 (1937).

of N^{15} compounds particularly well. The authors pointed out that by arranging several fractionating columns in cascade, such that a smaller second column operates on the produce from the first, etc., much higher concentrations could be secured in shorter times than would be the case if only *one* size of column were used throughout.

General Outlines of the Process

Such a cascade system of columns is represented diagrammatically in Fig. 1, and operates as follows: *F*cc of ammonium nitrate are fed into Unit 1, and if Unit 1 increases the concentration at the bottom by a factor, say 10, then 1/10 of *F*cc or *F'*cc of product from Unit 1 should be fed into the smaller column of Unit 2. The remaining 9/10 flow into a stripping column *S* where the ammonia gas is liberated by the addition of alkali and subsequent boiling, and returned through the column. If Unit 2 operating on the product from Unit 1 increases the concentration further by a factor of 10, then 1/10 of *F'*cc or *F''*cc of product from Unit 2 should be fed into the still smaller column of Unit 3, the remaining 9/10 flow into the stripper *S'* where the ammonia is liberated the same as before and sent back through the columns. The third unit then operates on the product from Unit 2, increasing the concentration further by, say, a factor of 10. Finally, the *F''*cc flow into stripper *S''* where all the ammonia gas is liberated and returned through the system. In this way the three units should change the ratio of the isotopes by a factor of 1000.

If the top part of a column is fed ammonium salt with known isotopic concentration, the transport can be calculated for this part of the column, and under conditions of total reflux is, $T=W(N-n)$ where W is the rate of flow per unit time, and N and n are the concentrations of N^{15} in the liquid and gas, respectively. Since equilibrium is established in this region,

$$\frac{N}{1-N}\Big/\frac{n}{1-n}=\alpha,$$

where α is the simple process factor, and hence

$$T=\frac{Wn(\alpha-1)(1-n)}{1+n(\alpha-1)}. \qquad (1)$$

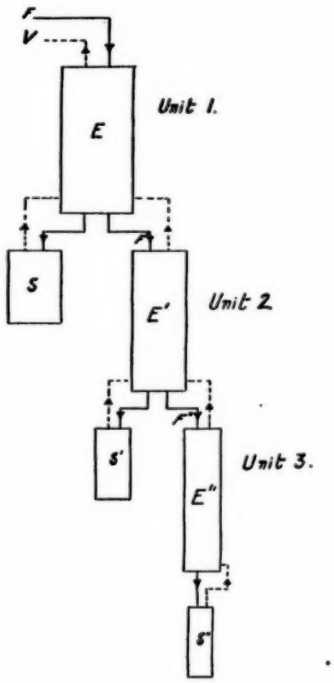

Fig. 1.

This equation applies until the columns come to a steady state, when the transport at each point is equal to zero. When N and n are both small and nearly equal,

$$T=WN(\alpha-1).$$

Since the flow of a unit is less by a factor, 10, than that of the preceding unit in the cascade and the concentration of the feed is about 10 times that of the preceding unit, the transport in each of the three units will be approximately the same as the system approaches a steady state. This is not quite true, however, since in the third unit of the system N and n are no longer small as compared to unity and T depends on $N(1-N)$ instead of N. This means that the rate of flow in Unit 3 should be somewhat larger than 10 times the rate of flow of Unit 2.

Huffman and Urey[2] have shown that the approach to the steady state in a single column operating without forward flow and with an infinite reservoir at one end is given by the formula

$$(1-N)\ln\frac{1-N}{1-N_0}+N\ln\frac{N}{N_0}=\frac{k\ln\alpha}{H}Kt, \qquad (2)$$

[2] Ind. and Eng. Chem. **29**, 531 (1937).

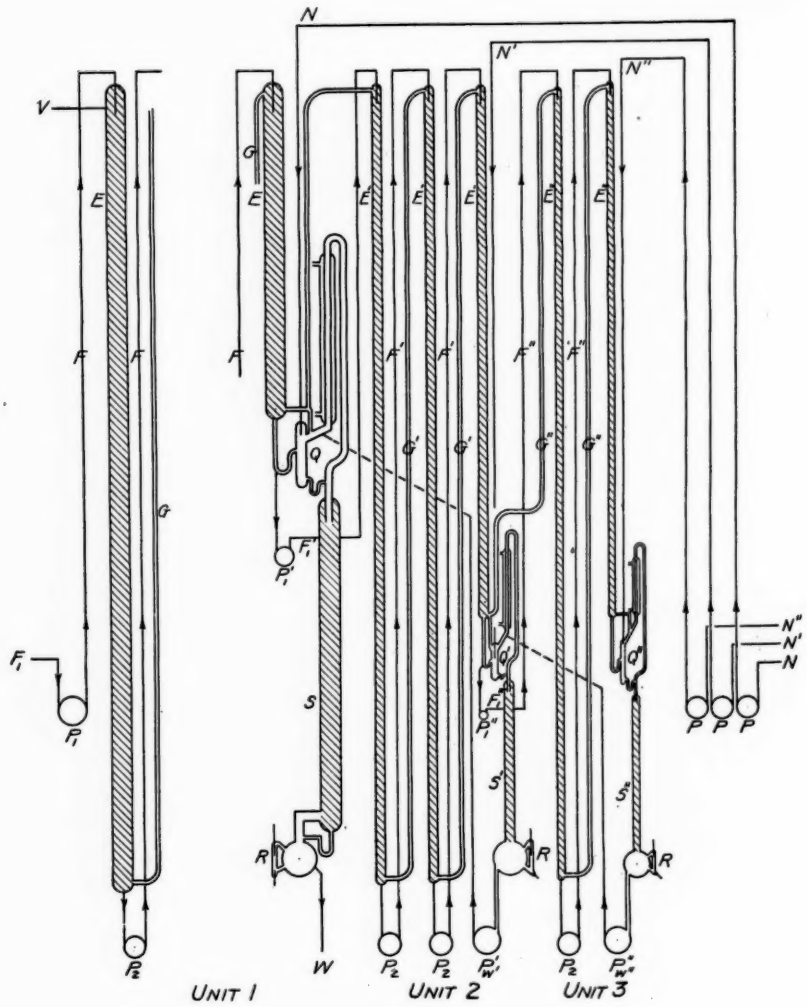

FIG. 2.

where N is the mole fraction of N^{15} in the feed material at one end of the column and N_0 the mole fraction N^{15} at the other end, H the amount of working material in the column during operation, t the time, and K the rate of transport. Then if Unit 1 in a cascade system of columns is operated alone until a steady state is reached with a tenfold increase in concentration, and if Unit 2, which has 1/10 the working material, and about the same rate of transport as Unit 1, is fed product from Unit 1, then it follows from Eq. (2) that Unit 2 will reach a steady state with a further tenfold increase in concentration in the same length of time as Unit 1.

Three units of the cascade system of columns were constructed. The results obtained with the two smaller units were reported in a previous communication.[3] The apparatus and further experiments are described below.

1. Apparatus

The actual apparatus is shown in Fig. 2. Unit 1 consists of 24 meters of glass column (7 cm inside diameter) packed with 6-mm Berl saddles. The column is mounted in five 4.5-meter sections and one 1.5-meter section. These sections are represented by the letters E in the diagram. Unit 2 consists of 12 meters of glass column (2.2 cm inside diameter) packed with 6-mm glass spirals of the Fenske type. This column is mounted in

[3] Thode, Gorham and Urey, J. Chem. Phys. 6, 296 (1938).

two 4.5-meter sections and one 3.0-meter section, E'. Unit 3 consists of 7.5 meters of glass column (1 cm inside diameter) packed with 5-mm glass spirals. This column is mounted in one 4.5-meter section and one 3-meter section, E''. The pump P_1 feeds ammonium nitrate solution into the top of the first section of Unit 1. P_1' pumps liquid product from a small reservoir at the bottom of Unit 1 into the top of the first section of Unit 2. P_1'' pumps liquid product from the bottom of Unit 2, into the top of the first section of Unit 3. Pumps, P_2, pump liquid as fast as it drains from the bottom of one section to the top of the next section to the right, through glass feed lines F, F' and F'', for the three units, respectively. The ammonium nitrate solution drains from the last section of each unit into small reaction chambers, Q, Q' and Q'' of Units 1, 2, and 3, respectively. Pumps P feed alkali solutions N, N' and N'' into the reaction chambers Q, Q' and Q'', respectively. The ammonia gas liberated and subsequently boiled out by the strippers passes back up through the sections. Glass tubes G, G' and G'' lead the gas from the tops of the sections to the bottoms of the preceding ones. Compressor C, to be discussed later, pumps the gas from Unit 2 to Unit 1. The ammonia gas escapes at V, and is carried to the drain by a stream of water passing through a packed column (8 cm inside diameter). A vacuum pump operated by a pressure regulated relay maintains a constant pressure at V. The column for removing the ammonia is placed between the vacuum pump and the point V.

S, S' and S'', are columns for stripping out ammonia gas for Unit 1, Unit 2, and Unit 3, respectively. S is a 1.5-meter glass column (7 cm inside diameter) packed with 1.2-cm glass Rashig rings. S' is a glass column (5 cm inside diameter), 1 meter long packed with 6-mm glass Rashig rings and S'' is a 1-meter glass column (3.7 cm inside diameter) packed with 6-mm glass Rashig rings. On the bottom of each stripping column is a copper boiler attached with three-ply rubber hose, and at the top are condensers for refluxing the water boiled. Regulators R, in the diagram consist of tungsten electrodes sealed into glass side arms. These regulators operate relays which in turn operate pumps Pw' and Pw''. In this way the waste liquid in the copper pots is kept at a convenient level. The copper pot is used as the second electrode of the regulator and the current at contact flows through the electrolytic solution. The waste liquid from Unit 3 is fed by pump Pw'' into the top of stripper S' and the waste from Unit 2 is fed by pump Pw' into the top of stripper S, and finally the waste of Unit 1, flows through a vacuum leg to a drain. By this arrangement any heavy ammonia not removed by the strippers S' and S'' is pumped back into the system.

The pumps, consist of two cylindrical rollers which rotate inside a brass cylinder and flex a rubber tube. This type of pump will pump gas as well as liquid, without the formation of a vapor lock. Its successful operation makes it possible to mount 45 meters of column on one floor. Pure gum rubber tubes, lubricated with castor oil are used in these pumps. The tube extends several feet on each side of the pump and is fastened at both ends to prevent it from working through or getting caught in the rollers. These pumps operate for several days without attention, and then it is only necessary to move the tubing through to a new position in the pump. This can be done while the pumps are in operation. Slight adjustments in the speed of the feed pump motors are necessary to maintain a constant rate of pumping. These motors are governor-controlled with variable speeds. If the pump becomes somewhat warmer than the solution, gas is generated from the solution saturated with gas in the rubber intake tube and gas is pumped with little or no liquid. When this happens we place the intake end of the tube in cool water, or lead the tube through a water cooled condenser. At the slightly lower temperature the gas phase disappears and the tube remains full of liquid. Some pumps are made with two and even three

TABLE I.

Run	Column			Rate of Feed cc per min.	N^{15} Enrichment Factor
	I.D. (cm)	Length (meters)	Packing		
1	1.0	1.2	5-mm glass spirals	0.65	1.42
2	2.2	1.3	6-mm glass spirals	2.5	1.29
3	2.2	1.3	6-mm glass spirals	6.3	1.32
4	2.2	1.3	6-mm Berl saddles	5.0	1.19
5	7.0	1.7	6-mm " "	50.0	1.22
6	7.0	1.7	6-mm " "	80.0	1.24

rubber tubes. One of these pumps takes the place of several where equal volumes of liquid are being pumped.

Before each run the columns are cleaned with cleaning solution and kept wet with distilled water until operations are started. It was found in test experiments that the commercial solutions of ammonium nitrate left an oily film in the columns. To eliminate this we filtered the solutions through charcoal and a cotton cloth bag.

In attempting to operate the three units at about 8 cm of mercury pressure certain difficulties were encountered. The pressure drop across the first unit was about 12 cm of mercury. Thus Unit 2 was operating at 20 cm of mercury instead of 8 cm. To overcome this difficulty a gas compressor was used between Units 1 and 2, operated by a pressure regulated relay. This compressor pumped ammonia gas from Unit 2 to Unit 1, and maintained Unit 2 at about 8 cm of mercury pressure.

Results

In these experiments with the glass columns, ammonium nitrate was used because of its high solubility (60 percent by weight) and also because of the high solubility of sodium nitrate. We used sodium hydroxide (33 percent by weight) without the precipitation of sodium nitrate in the waste.

A number of preliminary experiments at 8 cm of mercury pressure were made with columns 1 to 2 meters in length and of various diameters to determine their efficiency. Glass spirals and Berl saddles were tried as packing materials. The results are presented in Table I.

From a consideration of the above results, and using the equation

$$F=\alpha^{lk},$$

which expresses the enrichment factor F, for a distillation column in terms of the length l, we calculated the length of column required for each unit of our cascade to produce a tenfold change in isotopic concentration. The results of subsequent experiments with Units 2 and 3 are in good agreement with these calculations. However, Unit 1 was not found to be as efficient in the longer lengths, and it was necessary to increase its length from the estimated 15 meters to 24 meters before making the final run, and even then we did not secure the expected factor of 10.

The two smaller units were constructed first to test the efficiency of the longer lengths and to eliminate difficulties. For this experiment Unit 2 was fed 7.5 cc per minute of ammonium nitrate solution (60 percent by weight), and Unit 3, 0.85 cc per minute of liquid product from Unit 2. As in previous experiments the system was maintained at about 8 cm of mercury pressure. During the run ammonia gas samples were taken daily from the bottom of Unit 3, and the concentration of N^{15} determined with a Bleakney type of mass spectrometer, with the use of N_2 gas as previously described.[1] The results are presented in Table II.

Table II.

Time in Hours	Percentage N^{15}
0	0.38
48	0.95
96	1.9
144	3.4
192	5.3
230	6.9
278	8.8
316	12.9
354	14.8

In about 14 days we obtained 14.8 percent N^{15} and the concentration was continuing to rise. The two units were apparently working satisfactorily and the run was stopped since, with the addition of the larger first unit, we could produce ten times as much material as well as secure higher concentrations.

In the run using all three units 70 cc per minute of ammonium nitrate (60 percent by weight) was fed into Unit 1, 7.5 cc per minute of ammonium nitrate product from Unit 1 into Unit 2 and finally 0.85 cc per minute of ammonium nitrate product from Unit 2 into Unit 3. Because of the pressure drop through the first unit, it was difficult to maintain the system at 8 cm of mercury pressure as in previous runs. By maintaining 5 cm of mercury pressure at the first unit and 9 cm of mercury pressure at the second unit by means of the gas compressor previously described, we were able to maintain nearly the desired conditions. During the run, ammonia gas samples were taken from the three units each day and analyses made in the usual manner. In this run the apparatus was kept in operation with

total reflux until no further increase in concentration of N^{15} was apparently obtained. The final concentrations at the lower ends of the three units are given in Table III.

After the maximum concentrations were reached the apparatus was continued in operation for four days. In this time we produced 8.8 grams of 70.6 percent N^{15} by removing material from the system every twelve hours. Since this contains more N^{15} than the system transported in that length of time, the concentration is less than the maximum obtained. At the conclusion of the run each section was drained and washed separately and the nitrogen recovered as ammonium chloride.

At the maximum concentrations the three units transport according to formula (1), 1.3, 0.90 and 0.63 grams of N^{15} per twenty-four hours, respectively. Since Unit 1 gave an enrichment factor of 7 instead of the expected 10, the transports of the second and third units were low. When this first became apparent (during the run) the rate of flow in Unit 1 was decreased from about 70 cc to 60 cc per minute, thus decreasing its transport to about 1 gram N^{15} per 24 hours. The available transport of Unit 1 was decreased further by the accumulation of nitrogen equivalent to about 400 grams of ammonium chloride in the compressor between Units 1 and 2, an accumulation not discovered until the end of the run. This material is equivalent to a forward flow of the heavy constituent from Unit 1.

A serious interruption occurred during this run. The stripping column *S* cracked and a considerable amount of N^{15} was lost before the apparatus was stopped and repaired. Also, the alkali pumps stopped several times for a few minutes, resulting in the loss of concentrated material in the waste. However, very little N^{15} was lost by these minor interruptions as most of the waste containing concentrated material was saved and fed back into the top of stripping column *S*.

TABLE III.

UNIT	ENRICHMENT FACTOR	PERCENTAGE N^{15}
1	7.04	2.61
2	8.7	18.9
3	11.5	72.8
Over-all	702	

Altogether we operated forty days, in which time we produced material containing 31 grams of N^{15} in excess of the normal. This material includes the forward flow and all the drainage samples and ranges in concentration from 0.57 to 70.6 percent N^{15}.

We are indebted to the Research Corporation for grants covering the construction of the columns, to E. I. du Pont de Nemours & Company for the ammonium nitrate used in these experiments, and to the Carnegie Corporation for funds covering the purchase of other chemicals. In particular we wish to thank Dr. Irving Roberts for his assistance during the course of the operation of the column, and also Drs. John Clay, Clyde Hutchison, and John Gorham, for their help in the course of the experiments.

The Persistence of Molecular Vibration in Collisions

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The dispersion of sound is theoretically interpreted by the idea that the exchange of energy in collisions between molecular *translation* and *rotation* on one side and *vibration* on the other side is much slower than, for example, between the various translational degrees of freedom. It seemed desirable to find a direct optical method of observing this hypothetical effect. Apparatus has been developed in this laboratory for the purpose of investigating molecules present in very small concentration, like radicals, by their absorption spectra; with this method, relative concentrations of molecules are determined by comparing intensities of certain rotational lines. This test was applied to the higher vibrational levels of the I_2 molecule. Their concentration was artificially increased beyond the small amount present in thermal equilibrium by an electric discharge of brief duration. By varying the phase between an electric switch and optical shutter, snapshots of the absorption spectrum could be taken at different intervals after the discharge was interrupted. The result was that iodine molecules raised from the ground level to the first excited vibrational level are able to persist in this level through several thousand collisions with other iodine molecules before losing their vibration.

I. PROBLEM

THE dispersion of sound was discovered in 1925 by G. W. Pierce, who was working in the supersonic range. Since then it has been observed in various gases but only for molecules which at the temperature of the experiment have some vibrational energy levels excited. The velocity within the audible range does not depend upon the frequency; it is predicted by Einstein's theory of specific heats for gases with translational, rotational and some vibrational energy, like chlorine at room temperature. As the frequency of the sound is increased, a critical range is entered in which the velocity also increases. Above this critical range it is again constant and has the same value as that predicted by specific heat theory for gases with no excited vibration, such as hydrogen at room temperature. So the main result of the experiment may be described as follows: above a certain frequency range the molecular vibration apparently loses its share in the specific heat.

This effect is explained by Herzfeld and Rice[1] on the hypothesis that the molecular *vibration* requires a large number of collisions—more than *translation* or *rotation*—for reaching the value of thermal equilibrium after a sudden temperature change. The transmission of high frequency sound waves through a gas is accompanied by rapid changes of temperature, and with increasing frequency a range is reached at which the transfer of thermal energy of translation and rotation to energy of vibration fails to follow the rapid temperature changes. Instead, the energy of vibration assumes an average value determined by the average temperature. When this frequency is reached, the vibration no longer affects the velocity of the sound transmission, which consequently approaches the same value as that predicted for gases in which no vibration is excited. In recent years, on the basis of this theory, a great deal of work has been done, in particular by Knudsen and Kneser and by Eucken and his collaborators,[2] determining the persistence of molecular vibration by measurements of dispersion of sound.

It is desirable to find a more direct test for such a persistence of vibrations in collisions. Some spectroscopic experiments[2] on fluorescence radiation indicate such a persistence. All fluorescence experiments, however, deal with vibrating molecules *in an excited electronic level* colliding during their lifetimes with nonexcited molecules, whereas in dispersion of sound obviously no electronic excitation takes place. Therefore both types of experiment, acoustic and

* Now with The R.C.A. Institutes, Inc., Chicago. The experimental work reported here was done during the year 1936–37. As the investigation was interrupted before completion by the author going to Chicago, only a preliminary report is presented here.

[1] K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928).

[2] See the survey by O. Oldenberg and A. A. Frost, Chem. Rev. **20**, 99 (1937).

spectroscopic, do not directly compare. The case of greater practical importance is the normal electronic level. The reason is that its vibration is recorded in many chemical reactions as "energy of activation." Therefore its persistence in collisions is an important problem in chemical kinetics. It seems desirable to devise a spectroscopic experiment in which such a persistence of vibration of molecules *in their normal electronic level* is more directly observed. This seems feasible with a technique developed at this laboratory for a similar purpose, that is a test for free radicals which may be present in reacting gases in very small concentrations (0.003 mm).[3] They are observed by their absorption spectrum. The only difference is that in the present problem we are dealing with unstable molecules which rapidly disappear, not by their chemical reactivity—like radicals—but by deactivation in collisions.

A similar investigation for *rotation* of molecules was, incidentally, carried out by Frost and Oldenberg[3] in their investigation of the lifetime of free OH. No persistence of rotational energy in collisions could be observed by absorption spectra. For *vibration*, however, various arguments[2] point to a far more pronounced persistence.

The problem, therefore, is first to produce in a diatomic gas highly vibrating molecules by some kind of a brief shock and next trace their gradual disappearance by the fading with time of their absorption spectrum.

II. Experiment

Since by dispersion of sound chlorine gas was found to manifest a very great persistence of vibration (34,000 collisions at room temperature)[4] it seems advisable to do the spectroscopic investigation with the halogen that has the strongest absorption spectrum, that is, iodine. Its vapor pressure may be controlled by the temperature of a trap. It has the disadvantage, though, of being highly active and requiring extreme measures to prevent the formation of impurities.

The molecular absorption bands in the visible have been measured and classified by Mecke.[5] They consist of bands resulting from transitions originating in different vibrational levels in the lower electronic energy state. Each band has a complex rotational structure in which the distribution of intensities is determined by the temperature, and may be calculated from kinetic theory. Except for a small correction,[6] the absorption coefficient representing a rotational line is proportional, by Beer's Law, to the population of the energy level from which the line originated. Hence the rotational structure of a band gives us a set of absorption lines of which the ratio of intensities of any two lines is the same as the ratio of populations in the rotational energy levels giving rise to the two lines.

Two photographic plates taken of the absorption spectrum under different conditions are inserted in a comparator[7] which permits them to be observed side by side through a microscope. If in the first plate two rotational absorption lines in a certain vibration-rotation band represent transitions from rotational levels of which the populations are calculated to be as seven to five, say, and the later plate shows that the second line has increased in intensity and now compares with the first line of the first plate, then the population of the vibrational energy level giving rise to the band has increased in the ratio of seven to five, or 40 percent. Thus it is not necessary to measure the absolute intensities of the two absorption spectra as the rotational lines give us a set of graduated concentration marks.

The change of concentrations in the iodine vibrational energy levels was accomplished by an electric discharge of brief duration. By electron impact molecules are produced with electronic excitation and preferably high vibration as explained by the Franck-Condon rule. They radiate after a negligible lifetime, going back into the normal electronic state with normal rotation, but most of them with a considerable amount of vibration. (A very similar

[3] O. Oldenberg, J. Chem. Phys. **3**, 266 (1935). A. A. Frost and O. Oldenberg, J. Chem. Phys. **4**, 782 (1936). O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 439 (1938).

[4] A. Eucken, Oesterr. Chem. Ztg. **20**, 1 (1935).

[5] R. Mecke, Ann. d. Physik **71**, 108 (1923).

[6] Hill and Van Vleck, Phys. Rev. **32**, 250 (1928).

[7] A. A. Frost, D. W. Mann and O. Oldenberg, J. Opt. Soc. Am. **27**, 147 (1937).

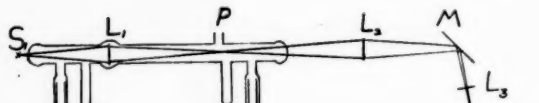

FIG. 1. Sketch of Apparatus. S_1, light source; L_1 and L_2, spherical glass lenses; P, tube to pump; T, iodine traps; M, plane mirror; L_3, cylindrical lens; S_2, slit of spectrograph; D, sector disk; R, revolving switch; I, thyratron interrupter; G, grating.

sequence of processes is excitation by light and the subsequent fluorescence radiation which shows by its spectrum the production of highly vibrating molecules in the normal electronic state). The increase in relative concentration of molecules in the first vibrational level with respect to the ground level was observed spectroscopically by the method previously described. This was done during the operation of the discharge and, furthermore, after interrupting the discharge, by snapshots at various time intervals selected by an optical shutter, in order to find the gradual loss of vibration through collisions. In order to produce an adequate density on the photographic plate this sequence of discharge and snapshot was periodically repeated.

Contamination by iodine of the mercury in the diffusion pump was guarded against by a trap surrounded by carbon dioxide snow and acetone. A spiralled copper sheet between the first trap and the pump provided additional protection from the iodine. The oil pump was protected from water vapor by activated alumina.

The vapor pressure was measured with a Coolidge bifilar quartz fiber manometer,[8] for which the writer is obliged to Professor A. S. Coolidge, who very kindly made available his original instrument. This proved highly satisfactory when used in the basement of the Research Laboratory, which is comparatively free from vibrations. Since it consisted only of Pyrex and quartz, it introduced no new impurities into the system from contamination by the iodine.

[8] Albert Sprague Coolidge, J. Am. Chem. Soc. **45**, 7 (1923).

It was necessary to work with a vapor pressure low enough so the number of collisions through which the vibration might persist would be spread over as long an interval as possible to facilitate observation, yet high enough to give a good absorption spectrum and a stable electric discharge through the tube. A pressure of three hundredths of a millimeter proved to be quite satisfactory. At this pressure the mean free path is about 0.6 mm, small enough so that the great majority of all collisions takes place between molecules, not with the wall. This vapor pressure was obtained by condensing the iodine into two traps maintained at a temperature of zero degrees Centigrade by surrounding them with crushed ice. The two traps were necessary, for clean-up in the discharge in iodine was so rapid that the iodine was removed faster than it could be replaced by evaporation from one trap.

The discharge and absorption tube (Fig. 1) had to be very long in order to provide light absorption in spite of the low vapor pressure; it was a Pyrex tube three meters long and five centimeters in diameter. The windows were bulbs made as thin as possible, but which nevertheless did introduce some astigmatism. To neutralize this an equal amount of opposite sign was developed by adjusting the external lens to a slight angle. Because of the unusual length of the apparatus it was impossible to mount the tube directly in front of the slit, so a plane mirror was used to reflect the light.

The internal lens was supported by three strips of glass cane about five centimeters long sealed to a short piece of tubing telescoped inside the main tube. A slight bulge in the tube permitted the discharge to pass around the lens. The electrodes were molybdenum cylinders about ten centimeters long and three centimeters in diameter. They were supported from the tungsten-Pyrex seal by heavy tungsten wire to prevent touching and fracturing the glass when heated in the baking out process by high frequency induction currents. Only tungsten and molybdenum were used in order to minimize the formation of impurities by the ionized iodine.[9] In order to protect the discharge tube from vapors that may be formed by the effect of

[9] Fruth, Phys. Rev. **31**, 615 (1928).

iodine on the stopcock grease, a magnetically operated glass valve separated the discharge tube from an ordinary glass stopcock lubricated with low vapor pressure Apiezon grease, which is practically immune from attack by iodine. Between the valve and the stopcock was connected a trap surrounded by carbon dioxide snow, which served to condense any iodine escaping through the glass valve.

The molybdenum electrodes were cleaned of gases and vapors by heating to incandescence with the Cruft Laboratory 2-kw High Frequency Bombarder. It was necessary to approach this high temperature in a number of successive steps, carefully pumping out all impurities released each time, so they would not attack the heated molybdenum and cause it to split along the edge. Unless the molybdenum was heated to this high temperature, a brownish impurity was formed rapidly by the iodine during the discharge.

The tube was degassed by successive discharges in helium followed by pumping of the helium and the impurities released during the discharge. The process was repeated until the helium spectrum remained unchanged after a lengthy discharge. Relatively pure helium was available and this was further purified by passing slowly through a carbon trap surrounded by liquid air, the carbon first having been treated to a long pumping while maintained at a temperature as high as the Pyrex would stand. When the tube had been thoroughly degassed, C.P. iodine was fractionated over from a side tube.

A synchronous motor was geared down to a shaft on which rotated a brass and Bakelite sector disk. This served as a switch operating a Thyratron (FG29) in the primary circuit of the discharge transformer. An optical sector cardboard disk rotated on the same axis with the switch. The apparatus was mounted inside the grating room with the cardboard disk just behind the slit. By varying the phase between electrical and optical sectors, snapshots could be taken of the iodine absorption spectrum at different time intervals after interrupting the discharge.

The spectra were photographed in the second order of a twenty-one-foot Rowland grating. A five hundred-watt Mazda projection lamp served as light source for the absorption spectrum. Pre-exposed Eastman Type 144D plates were used, as this emulsion when sensitized for the red has a sensitivity corresponding to Type III with a contrast corresponding to Type IV. The exposure time was considerably reduced by a cylindrical lens which concentrated on the slit light that otherwise would have been lost. A slit width of 25 microns was used.

The rotating disk had two 22.5° openings separated by 180°. It was operated from an 1800-r.p.m. synchronous motor, geared down by a ratio of sixteen to one. Exposures of the order of an hour, including intermissions, were necessary. This corresponded to a continuous exposure of 7.5 minutes. The final image was the cumulative result of about 13,500 snapshots of 0.033 seconds each.

A photographic plate of the normal iodine absorption spectrum was split lengthwise and the two halves placed in the comparator. This instrument was specially built for the purpose of selecting from two spectra absorption lines of equal intensity. Two equal rotational lines, one belonging to a transition originating in the ground vibrational level and one belonging to a transition originating in the first excited vibrational level, were selected. They served as reference lines for thermal distribution. Any divergence from thermal distribution caused a relative change in absorption by the vibrational levels responsible for these two lines, and they no longer matched.

III. Result

The plates taken while the discharge was passing through the absorption tube showed, when split and observed in the comparator, that these two lines were no longer of equal intensity, the one originating in the first excited vibrational level now being the stronger. The shift in relative intensities was not large, but it was quite clear and definite. This showed directly an increase in relative population of the first excited vibrational level with respect to the ground level caused by the discharge.

Repetition of the experiment more than a score of times showed that optimum values for the discharge were about 12,000 volts at 100 milliamperes. Much increase in the current

caused excessive dissociation which made comparison of the spectra difficult, while smaller currents gave less excitation and therefore reduced the shift of relative intensities.

Snapshots of the absorption spectrum taken at different intervals after the discharge was interrupted showed that the increase perceptibly persisted for at least a thirtieth of a second. Under the conditions of the experiment, this corresponded to seven thousand collisions between iodine molecules. This gave a direct spectroscopic confirmation of the hypothesis of the persistence of vibration in collisions proposed by Herzfeld and Rice in their theory of the dispersion of sound.

The method described here offers the advantage of giving the *most direct evidence* for the persistence of vibration in collisions. However, it does not lend itself to a *quantitative* treatment as well as the dispersion of sound method. The reason is that each vibrational level above the normal level not only *loses* concentration by the general slow approach to the thermal distribution, but at the same time it registers a certain *gain* coming from higher vibrations. We observe a difference of two effects that cannot easily be treated quantitatively.

In conclusion, the author takes great pleasure in expressing his gratitude and appreciation to Professor O. Oldenberg, who proposed and guided this investigation, for his cooperation and encouragement. He wishes also to acknowledge his indebtedness to Professor E. Leon Chaffee and to Dr. W. M. Preston for their helpful suggestions, and to Mr. H. L. Leighton for his excellent glass blowing.

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The Equilibrium Dissociation and Thermodynamic Constants of Nitrosyl Chloride. Comparison with Spectroscopic Data

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Careful measurements of the equilibrium dissociation of nitrosyl chloride into nitric oxide and chlorine have been made in the temperature range 100–220°. Pressure-temperature measurements at 0°–100° on mixtures of nitrosyl chloride and nitric oxide were made and from them the second virial coefficients of nitrosyl chloride gas were calculated. These vary from -389 cm³/mole at 0° to -196 cm³/mole at 100°. The virial coefficients were used to correct the measured equilibrium constants to those for perfect gases. Equations for free energy, entropy and heat content changes accompanying the dissociation were derived as functions of the temperature. The experimentally found entropy changes for the reaction were found to be less than those calculated from spectroscopic data by 3.61 ± 0.3 cal./deg. To attain agreement, the spectroscopic entropy of nitrosyl chloride must be increased by 1.8 cal./deg., and this was attained by assuming that an observed infra-red frequency at 923 cm^{-1} is a combination, $633+290$ cm^{-1}. For the reaction $2NOCl(g) = 2NO(g) + Cl_2(g)$, $\Delta F°_{298} = 9{,}720 \pm 60$ cal., $\Delta S°_{298} = 28.0 \pm 0.5$ cal./deg. $\Delta H°_{298} = 18{,}060 \pm 200$ cal. $S°_{298}(NOCl) = 63.0 \pm 0.3$ cal./deg.

INTRODUCTION

THE dissociation of nitrosyl chloride, NOCl, into nitric oxide and chlorine under equilibrium conditions has been studied by several investigators, but only the work of Dixon[1] lays claim to any accuracy. Dixon's results are subject to some uncertainties in the temperature scale ($\pm 2°$), the measurements, and the effect of gas imperfections, so that comparisons with the thermodynamic quantities calculated from molecular and spectroscopic data, while suggestive, are not altogether satisfying. Recently, and after the present investigation was nearly completed, Jahn,[2] employing the electron diffraction results

[1] Dixon, Zeits. f. physik. Chemie Bodenstein Festband, 679 (1931).

[2] Jahn, J. Chem. Phys. **6**, 335 (1938).

of Ketelaar and Palmer[3] and the infra-red spectrum determined by Bailey and Cassie,[4] showed that between the predictions of theory and Dixon's measurements there is a discrepancy that seems definitely greater than that caused by errors in the measurements. To account for the discrepancy, Jahn suggested that nitrosyl chloride might exist in a triplet normal state and perhaps also a low lying singlet state so that its calculated entropy could be increased by $R \ln 4$. He made the justifiable assumption that the difficulty does not arise from a lack of precise knowledge concerning nitric oxide and chlorine; the spectroscopic and thermal data for nitric oxide have been analyzed carefully by Johnston and Giauque,[5] Johnston and Chapman,[6] and Johnston and Weimer.[7] The assumption of a triplet state requires that the substance be paramagnetic. Although liquid nitrosyl chloride is known to be diamagnetic,[8] Beeson and Coryell[9] made further experiments on the gas and found it to be diamagnetic also. Accordingly no degeneracy of the kind associated with paramagnetism can be invoked in the case of gaseous nitrosyl chloride.

In the present paper are described the results of experiments on the equilibrium reaction

$$2NOCl(g) = 2NO(g) + Cl_2(g) \qquad (1)$$

in the temperature range 100°–220°C. In order to make the comparison of the results with theory significant, very pure materials were used and accurate measurements were made. Since the gases are not perfect, additional experiments were made to determine the magnitude of the imperfections. As will be shown below, these accurate measurements are not in accord with the predictions of the theory unless one is justified in giving a different interpretation to the infra-red absorption spectrum than that offered by Bailey and Cassie.

[3] Ketelaar and Palmer, J. Am. Chem. Soc. **59**, 2629 (1937).
[4] Bailey and Cassie, Proc. Roy. Soc. **A145**, 336 (1934).
[5] Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929).
[6] Johnston and Chapman, J. Am. Chem. Soc. **55**, 153 (1933).
[7] Johnston and Weimer, J. Am. Chem. Soc. **56**, 625 (1934).
[8] Wilson, J. Am. Chem. Soc. **56**, 747 (1934).
[9] Beeson and Coryell, J. Chem. Phys. **6**, 656 (1938).

Preparation of Materials

Chlorine. Tank chlorine was purified as follows. The gas was passed into ice-cold distilled water until most of the latter had been converted into chlorine hydrate, $Cl_2 \cdot 8H_2O$. The temperature was then raised to about 10°, and the chlorine evolved, after passing through reagent grade anhydrous calcium chloride, was condensed into weighed glass capsules. The apparatus used was entirely of glass and the chlorine did not come in contact with rubber or other organic substances. The first portions of chlorine were rejected. Analysis showed that the final product in the sealed glass capsules contained less than 0.1 percent of hydrogen chloride.

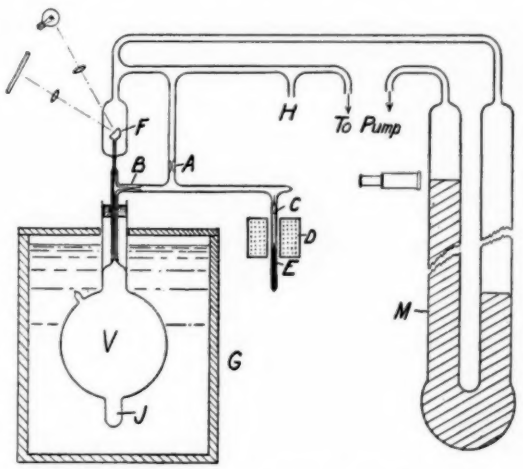

Fig. 1. Reaction vessel and auxiliary apparatus, (not to scale).

Nitric Oxide. The nitric oxide was prepared by a slight modification of the method described by Johnston and Giauque.[5] The gas was stored at about atmospheric pressure in flasks which had been carefully baked out under vacuum for several hours.

Experimental Methods, Precision of Measurements and Corrections

Apparatus and procedure

The apparatus[10] is shown diagrammatically in Fig. 1. V is a Pyrex glass reaction vessel of 1049.7 ml capacity at 20°C. G is a thermostat

[10] Blair, Brass and Yost, J. Am. Chem. Soc. **56**, 1916 (1934).

TABLE I. *Initial amounts and pressures of reactants. Volume of the reaction vessel,* 1049.7 ml: *volume of the dead space,* 2.3 ml: *volume of the side arm,* 23.8 ml.

Run	wt. Cl_2 g	Nitric Oxide: Pressure Int. cm Hg at 0°	Nitric Oxide: Temp. °C	Nitric Oxide: Vol. ml	Approx. Mole Ratio NO/Cl_2
III	0.7397	40.51	19.95	1075.8	2.29
IV	0.8518	30.59	18.88	1075.8	1.50
V	0.7611	37.58	22.00	1075.8	2.04

containing hydrogenated cottonseed oil.[11] The reaction vessel was attached to a Pyrex glass click gauge[12] *F* by means of capillary tubing. The capsule *C*, containing a weighed amount of chlorine, was provided with an easily breakable tip which could be broken off by the glass enclosed, magnetically operated, iron hammer *E*.

Before admitting the gases, the reaction vessel was baked out under high vacuum, allowed to stand evacuated overnight, and again baked out under high vacuum. After cooling, nitric oxide at a convenient pressure was admitted at *H* and the system sealed off at *A*. With the thermostat at room temperature the pressure of the nitric oxide was measured. The thermostat was then removed and the nitric oxide condensed by means of liquid air into the tube *J*. The chlorine *C* was frozen by means of liquid air and the tip of the capsule broken. On removing the liquid air the chlorine vaporized and condensed in the tube *J*. Finally the side arm was sealed off at *B*, and the nitric oxide and chlorine were allowed to vaporize into the reaction vessel.

The volumes of the side arm, 23.8 ml, and the click gauge and capillary tubing, 2.3 ml, were determined at appropriate times and were taken into account in calculating the amount of nitric oxide in the reaction vessel.

The temperature of the thermostat was maintained constant to within ±0.1° by means of a glass-enclosed mercury thermoregulator which contained hydrogen in the space where electrical contact was made or broken. No fouling of the mercury surface occurs in such a regulator if it is carefully freed from oxygen by heating under vacuum before admitting the hydrogen.

Equilibrium pressure measurements were made as follows. Beginning at 100° the temperature of the thermostat was maintained constant for several hours until it was certain that the pressure in the reaction vessel was undergoing no further change. This pressure was then measured. The temperature of the thermostat was raised 10° for one hour, then lowered to the original temperature, and the pressure again measured after it had become constant. This procedure was followed at 10° intervals in proceeding to higher temperatures. In proceeding down the temperature scale, equilibrium was again approached from both the high and low temperature side at each temperature chosen for measurements.

It was found easy to bring the thermostat to any predetermined temperature, and this made it possible, in going down the temperature scale, to carry out measurements at the same temperatures used when going up the scale. Accordingly, for each temperature, four final pressure measurements were made. These did not differ by more than 0.02 cm. The same temperatures were also chosen for the different runs.

Precision of measurements

The thermoregulator maintained the temperature of the thermostat constant to within ±0.1°. Temperatures were measured to ±0.05° with mercury thermometers which were calibrated periodically against thermometers from the National Bureau of Standards.

The mercury manometer used had an inside diameter of 2.15 cm. It was enclosed in a case whose front and sides were, respectively, of plate and window glass. Two thermometers served to determine the temperature of the mercury and of the air in the nonevacuated limb. Pressure measurements were made with a cathetometer whose scale was calibrated against a standard decimeter, ruled on glass, from the National Bureau of Standards. Pressure measurements could be duplicated to within ±0.005 cm.

[11] The fumes from hot cottonseed oil have been found to be irritating and possibly harmful to the eyes and lungs. Care should therefore be exercised in the use of this substance.

[12] The outer surface of the click gauge was silver-plated. By means of lenses, light was made to converge at the mirror-like surface from which it was reflected to a screen. The reflected pattern varied with the position of the membrane in such a way as to facilitate greatly the use of the gauge. Measurements with the gauge used were reproducible to less than ±0.005 cm.

Corrections applied to all recorded data

Corrections were made to take account of the following items: (1) the thermal expansion of the Pyrex glass reaction vessel (the coefficient of expansion given in I.C.T.[13] was used), (2) the exposed stem of the thermometer (stem correction), (3) the almost negligible amount of nitric oxide present in the side arm when it was sealed off, (4) the quite small effect on the pressure caused by changes in temperature of the air in the unevacuated limb of the manometer during measurements, (5) the height of the menisci[14] and the temperature of the mercury in the manometer, and (6) the acceleration caused by gravity.[15]

At Pasadena $g=979.57$ cm/sec.^{2}. The standard is $g=980.67$ cm/sec.^{2}. Accordingly all pressure measurements recorded in the tables are in international centimeters of mercury[16] at 0°.

In addition to these corrections, correction for the room temperature dead space (obnoxious volume) in the click gauge was also made. To do this it was assumed that the dead space contained only nitrosyl chloride and nitric oxide or chlorine depending on which of these was present in excess. This assumption is justified for correction purposes since at room temperature only some 0.5 percent of the nitrosyl chloride at atmospheric pressure is dissociated. If, in the dead space, $(N°_{NO})_2$ is the number of moles of NO plus the number of moles of NOCl, and $(N°_{Cl_2})_2$ is the number of moles of Cl_2 plus half the number of moles of NOCl, then it is easy to show that with excess NO

$$(N°_{NO})_2=PV_2/RT_2 \qquad (2)$$

with excess Cl_2

$$(N°_{NO})_2=PV_2 2A/RT_2(A+2) \qquad (3)$$
$$A=(N°_{NO})_2/(N°_{Cl_2})_2,$$

where V_2 is the volume (2.3 ml) of the dead space, T_2 its temperature, and P the pressure. At each temperature the quantities $(N°_{NO})_2$ and $(N°_{Cl_2})_2$ are subtracted from the initial amounts of nitric oxide and chlorine respectively placed in the reaction vessel.

Results of the Equilibrium Measurements

Three separate fillings of the reaction flask were made, one with excess nitric oxide, one with excess chlorine and one with equivalent amounts. The initial amounts and pressures are presented in Table I. In Table II are given the observed equilibrium pressures, P, in international cm of Hg at 0°, and the values of log K'_{cm} and log K_{cm}. K' was calculated from the following relation

[13] *International Critical Tables* (1929) Vol. II, p. 93.
[14] *International Critical Tables* (1929) Vol. I, p. 73.
[15] *International Critical Tables* (1929) Vol. I, p. 68.
[16] *International Critical Tables* (1929) Vol. I, p. 69.

TABLE II. *Results of equilibrium measurements.* 0°C = 273.10°K, $K=P^2_{NO}P_{Cl_2}/P^2_{NOCl}$.

	Run III			Run IV			Run V		
°K	P*	$-\log_{10} K'_{cm}$**	$-\log_{10} K_{cm}$†	P	$-\log_{10} K'_{cm}$	$-\log_{10} K_{cm}$	P	$-\log_{10} K'$	$-\log K$
372.38	52.49	a	2.538	—	—	—	—	—	—
372.67	—	a	—	46.64	3.094	2.569	49.03	2.850	2.586
381.52	53.83	—	2.383	—	—	—	—	—	—
382.50	—	—	—	48.00	2.654	2.306	50.56	2.509	2.312
392.31	55.50	2.473	2.080	49.38	2.309	2.062	52.16	2.181	2.032
402.11	57.06	2.054	1.837	50.82	1.990	1.812	53.78	1.916	1.795
411.86	—	—	—	52.31	1.695	1.564	55.45	1.656	1.558
412.17	58.80	1.687	1.549	—	—	—	—	—	—
422.62	60.67	1.400	1.299	54.03	1.395	1.302	57.39	1.377	1.299
432.50	62.50	1.166	1.088	55.59	1.190	1.114	59.22	1.152	1.087
442.34	64.42	0.9358	0.8749	57.27	0.9611	0.9011	61.09	0.9362	0.8838
452.13	66.39	0.7275	0.6785	58.99	0.7506	0.7022	63.04	0.7265	0.6828
461.93	68.44	0.5323	0.4933	60.78	0.5538	0.5139	65.03	0.5364	0.4986
471.71	—	—	—	62.61	0.3713	0.3390	67.08	0.3551	0.3232
481.46	—	—	—	—	—	—	69.19	0.1767	0.1486
491.24	—	—	—	—	—	—	71.35	0.0120	−0.0122

* P = Equilibrium pressures in Int. cm Hg at 0°.
** $\log_{10} K'_{cm}$ refers to actual gases.
† $\log_{10} K_{cm}$ refers to perfect gases.
a The values of $\log_{10} K'_{cm}$ are imaginary.

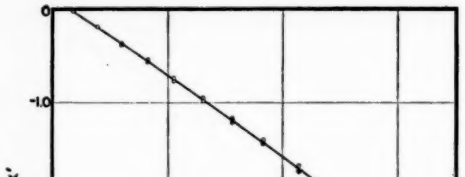

FIG. 2. Plot of log K' (assuming all gases perfect) against $1/T$.

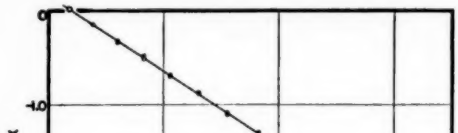

FIG. 3. Plot of log K (corrected for gas imperfections) against $1/T$. The solid line was plotted from Eq. (12). Each circle represents one or more experimental values.

derived from the perfect gas laws.

$$K'_{cm}=(P^{\circ}_{NO}-2\Delta P)^2(P^{\circ}_{Cl_2}-\Delta P)/4\Delta P^2, \quad (4)$$

where P°_{NO} is the pressure of nitric oxide which would have existed at the temperature in question if no reaction had taken place, $P^{\circ}_{Cl_2}$ is the corresponding pressure of chlorine, and $\Delta P=P^{\circ}_{NO}+P^{\circ}_{Cl_2}-P$. The value of the gas constant used was $R=6236.6$ ml cm/mole deg. and it was calculated from the I.C.T.[17] value $R=82.06$ ml atmos./mole deg. Inasmuch as the gases involved are not perfect, additional experiments, to be described below, were made to determine the extent of the imperfections, and the results were used in arriving at $\log K$. K refers, therefore, to perfect gases.

At the higher temperatures the values of K' differ from the mean by ± 3 percent or less. This agreement can be considered as excellent. At the lower temperatures, and when one of the reactants is in excess, considerable difference in the values of K' is to be noted. Most of this difference arises from the fact that considerable errors in P_{Cl_2} or P_{NO}, especially when these are small, result from their calculation as differences in large pressures.

If the gases present at the larger pressures were perfect, the errors in P_{NO} or P_{Cl_2} would correspond only to the experimental error, but since the partial pressure of a gas present at a relatively high pressure as calculated from the perfect gas laws is not equal to its true pressure, it follows that a small pressure found by taking the difference between two large pressures will be in error by an amount much greater than that of the measurements. The main effect of the corrections for gas imperfection is that on the values of P_{Cl_2} and P_{NO}. At *low temperatures* the values of K' are very sensitive to the corrections and to errors in the measurements; the corresponding values of K are less sensitive since the effect of the corrections for gas imperfections is to make the small uncorrected pressures larger.

For the purposes of thermodynamics the fugacities of imperfect gases must be used in evaluating the equilibrium constants. In the present case it was found, as might be expected, that K_f, $K_{p(\text{real})}$ and $K_{p(\text{ideal})}$ differed but little. Thus at 422.6°C the difference is less than 0.5 percent, well within the allowed error. The correction of the thermodynamic quantities to the ideal gas state is also less than the small experimental errors in these quantities. Accordingly we can consider K, which was calculated using corrected pressures, as referring to the ideal gases. In Fig. 2 is shown a plot of $\log_{10} K'$ against $1/T$ and in Fig. 3 the corresponding plot for $\log_{10} K$, where K refers to perfect gases. It will be noted in the latter figure the points for the three runs show but little scattering over the whole temperature range investigated. At 471.74° Dixon's value for K' differs from that in the table by about 7 percent.

DETERMINATION OF THE GAS IMPERFECTIONS

The materials and experimental procedure were the same as those in the equilibrium measurements. An excess of nitric oxide was always added to repress the dissociation of the nitrosyl chloride. Over the temperature range 0°

[17] *International Critical Tables* (1929) Vol. I, p. 18.

to 100° the pressures of mixtures of accurately known amounts of nitric oxide and chlorine were measured. In Table III are shown the initial amounts and pressures of chlorine and nitric oxide. Table IV contains the observed temperatures and pressures, as well as ΔP the difference between the observed pressure corrected for the imperfection of nitric oxide, and the pressure calculated for a mixture of perfect gases. Nitric oxide alone shows but little gas imperfection,[7] and it proved convenient to take this into account in arriving at the values of ΔP. Corrections were also made for the small equilibrium pressure of chlorine present, about 0.01 cm or less.

The equation of state of a pure imperfect gas over a limited range of temperatures and pressures can be taken as

$$P-NRT/V=NBP/V, \qquad (5)$$

where B is the second virial coefficient and is a function of the temperature. In the correction term on the right P may, to a good approximation, be replaced by NRT/V so that

$$P-NRT/V=BN^2RT/V^2=B\bar{N}^2RT, \qquad (6)$$

where $\bar{N}$ is the number of moles per unit volume. For a mixture of n imperfect gases $\bar{N}=\bar{N}_1+\bar{N}_2+\cdots\bar{N}_n$. It will be assumed that B is a function of $\bar{N}_1, \bar{N}_2, \cdots\bar{N}_n$ such that the correction term $C=B\bar{N}^2RT$ will be given by

$$C_{1,2\ldots n}=RT\sum_i^n\sum_j^n B_{ij}\bar{N}_i\bar{N}_j. \qquad (7)$$

B_{ij} is a measure of the interaction between the i and j molecules, and when $i=j$ B_{ij} is the second virial coefficient for the pure gas j. B_{ij} will be assumed, as seems likely, to be a function of B_{ii} and B_{jj} of such a kind that B_{ij} will be the mean of B_{ii} and B_{jj}. Of the various kinds of means, $B_{ij}=(B_{ii}B_{jj})^{\frac{1}{2}}$ seems, for physical reasons, less acceptable than $B_{ij}=(B_{ii}+B_{jj})/2$, since in the former case B_{ij} becomes vanishingly small when one of the gases is nearly perfect. The molecules of a gas which, by itself, is nearly perfect may well show appreciable interaction with the molecules of an imperfect gas. Accordingly, the final expression for $C_{1,2\ldots n}$ becomes, on dropping superfluous subscripts,

$$C_{1,2\ldots n}=\frac{RT}{2}\sum_i^n\sum_j^n(B_i+B_j)\bar{N}_i\bar{N}_j. \qquad (8)$$

Johnston and Weimer[7] have studied the imperfections of nitric oxide and Eucken and Hoffman[18] have made a similar study of chlorine. Nitric oxide shows comparatively little imperfection in the temperature range of interest, B_{NO} being about 10 percent of B_{Cl_2} or B_{NOCl}. For this reason the small imperfections of nitric oxide have already been taken into consideration in the calculation of ΔP from the experimental data.

Since B_{NO} is small and $B_{NO,NOCl}=(B_{NO}+B_{NOCl})/2$, $B_{NOCl}=2B_{NO,NOCl}$ to a good approximation. In Table V are presented the values of $-B_{NOCl}$ for even temperatures calculated from smooth curve values of ΔP under the assumptions

TABLE III. *Initial amounts and pressures of chlorine and nitric oxide.*

VOL. SIDE ARM 19.6 ml IN RUN II; 21.4 ml IN RUN IV					
		NITRIC OXIDE			
RUN	WT. Cl_2 g	PRESSURE INT. cm Hg AT 0°	TEMP. °C	VOL. ml	APPROX. INITIAL MOLE RATIO NO/Cl_2
II	0.6924	52.66	24.96	1071.6	3.11
IV	0.8169	58.96	27.96	1073.4	2.92

TABLE IV. *Results of the experiments to determine gas imperfections.*

	RUN II		RUN IV	
°K	P. INT. cm Hg, 0°	ΔP cm	P. INT. cm Hg, 0°	ΔP cm
372.67	66.76	0.25	74.10	0.30
348.04	62.32	.28	69.17	.34
323.09	57.87	.27	64.20	.35
298.12	53.34	.32	59.20	.38
276.03	49.35	.35	54.73	.45

TABLE V. *The second virial coefficients of nitrosyl chloride.*

	$-B_{NOCl}$ IN cm³/MOLE			
t°C	RUN I	RUN II	MEAN	$-B_{Cl_2}$
100	202	191	196	135
75	224	212	218	169
50	260	245	253	215
25	314	300	307	274
0	398	380	389	343

[18] Eucken and Hoffman, Zeits. f. physik. Chemie **B5**, 442 (1929).

set forth above. For comparison the values of $-B_{Cl_2}$ are also included in the table. The values of B_{NOCl} are of the same order of magnitude as those of B_{Cl_2} but larger, and this is to be expected since nitrosyl chloride has the higher boiling point, $-5.7°$. The error in B_{NOCl} is about 7 percent.

The values of B_{NOCl} were plotted and the plot extrapolated to 200° (where $B_{NOCl}=-116$ cm³/mole), and the extrapolated values, together with those for B_{Cl_2} and B_{NO}, were used in connection with Eq. (8) to arrive at the corrections applied to the results of equilibrium measurements. The corrections were made by a process of successive approximations, the second approximation usually sufficing. By far the greater part of the correction is due to the imperfection of nitrosyl chloride since this gas was always present at relatively high pressures.

The Thermodynamic Quantities Calculated from the Experimental Results

When $\log K$ is plotted against $1/T$ the resulting curve is, within the limits of error (from less than ±3 percent to ±4 percent), a straight line. This fact indicates that ΔC_P for the reaction $2NOCl(g)=2NO(g)+Cl_2(g)$ is small. Since ΔC_P could not be determined from the curvature of the $\log K$, $1/T$ curve, it was evaluated, as a function of T, from spectroscopic data. To this end use was made of published data on the heat capacities and entropies of nitric oxide[6] and chlorine[19] together with the vibrational frequencies (1888 cm^{-1} for NO, 570 cm^{-1} for Cl_2) of these molecules, to construct semi-empirical equations for C_P. The fundamental nondegenerate frequencies,[4] 633 cm^{-1}, 923 cm^{-1} and 1832 cm^{-1}, of nitrosyl chloride were employed to arrive at an expression for C_P for this substance. The final result for ΔC_P is

$$2NOCl(g)=2NO(g)+Cl_2(g),$$
$$\Delta C_P^\circ=8.237-0.021416T+14.525\times10^{-6}T^2\pm0.01 \text{ cal./deg.} \quad (9)$$

This yields for ΔC_P, 3.14 cal./deg. at 298.1°K, 1.99 cal./deg. at 400°K and 1.16 cal./deg. at 500°K, and shows that, in agreement with experiments, ΔC_P is small.

[19] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

From the slope of the $\log K$, $1/T$ curve a value of ΔH was determined. This when combined with ΔC_P yields the formula

$$\Delta H^\circ=16429+8.237T-0.010708T^2+4.8417\times10^{-6}T^3\pm180 \text{ cal.} \quad (10)$$

Finally the equations for ΔF°, $\log_{10} K$ and ΔS may be established and are, respectively,

$$\Delta F^\circ=16429-18.967T\log_{10}T+21.452T+0.010708T^2-2.4208\times10^{-6}T^3\pm40 \text{ cal.}, \quad (11)$$

$$\log_{10}K_{cm}=-2.808-3591.0/T+4.1457\log_{10}T-0.0023406T+0.52915\times10^{-6}T^2\pm0.02, \quad (12)$$

and

$$\Delta S^\circ=-13.215+18.967\log_{10}T-0.021416T+7.2625\times10^{-6}T^2\pm0.3 \text{ E.U.} \quad (13)$$

It is to be emphasized that spectroscopic data have been used here only in arriving at an expression for ΔC_P. In Fig. 3 the solid curve was plotted from the above equation for $\log_{10} K$; the circles indicate experimental values. The equation, within the limits of error, agrees with experiment throughout the temperature range investigated. Since ΔC_P is small, agreement would still result if this quantity were altered by as much as 50 percent.

From the above equations, and from the published values for the entropies at 25° of nitric oxide,[6] 50.35 cal./deg. and chlorine,[19] 53.31 cal./deg., the following thermodynamic quantities were calculated.

$$2NOCl(g)=2NO(g)+Cl_2(g),$$
$$\Delta F^\circ_{298}=9{,}720\pm60 \text{ cal.},$$
$$\Delta H^\circ_{298}=18{,}060\pm200 \text{ cal.},$$
$$\Delta S^\circ_{298}=28.0\pm0.5 \text{ cal./deg.},$$
$$S^\circ_{298}(NOCl)=63.0\pm0.3 \text{ cal./deg.}$$

Comparison with Spectroscopic Data

The entropies of nitric oxide and chlorine have been calculated from spectroscopic data, by Johnston and Chapman[6] and Giauque and Overstreet.[19] From their results the following semi-empirical equations were derived.

$$S^\circ_{NO}=7/2R\ln T+S_{1888}+10.787 \text{ E.U.}, \quad (14)$$

$$S_{Cl_2}=7/2R\ln T+S_{570}+13.180 \text{ E.U.}, \quad (15)$$

where S_ω is the entropy associated with the vibrational frequency ω.

The moments of inertia of nitrosyl chloride, referred to principal axes, as calculated from Ketelarr and Palmer's[3] electron diffraction results are, $I_1=8.99\times10^{-40}$g cm^2, $I_2=146.8\times10^{-40}$g cm^2 and $I_3=155.8\times10^{-40}$g cm^2. The interatomic distances given by them are N−O 1.14±0.02A, and Cl−N 1.95±0.01A, and the bond angle Cl−N−O is 116±2°. Bailey and Cassie's[4] infrared study led them to the conclusion that the fundamental frequencies of nitrosyl chloride were $\omega_1=1832$ cm^{-1}, $\omega_2=633$ cm^{-1} and $\omega_3=923$ cm^{-1}. ω_2 represents the bending frequency. From these data there was derived the relation

$$S^\circ_{NOCl}=4R\ln T+S_{633}+S_{923}+S_{1832}+15.460 \text{ E.U.} \quad (16)$$

and finally the purely empirical relation

$$\Delta S(\text{spectr.})=-9.605+18.967\log_{10}T-0.021416T+7.2625\times10^{-6}T^2\pm0.01 \text{ E.U.} \quad (17)$$

The experimentally found relation is

$$\Delta S(\text{expt.})=-13.215+18.967\log_{10}T-0.021416T+7.2625\times10^{-6}T^2\pm0.3 \text{ E.U.} \quad (13)$$

A comparison of the spectroscopic and experimental values of ΔS shows immediately that

$$\Delta S(\text{spect.})-\Delta S(\text{expt.})=3.61\pm0.3 \text{ E.U.} \quad (18)$$

that is, a discrepancy of 3.61±0.3 cal./deg. which is, within the limits of error, independent of the temperature. This is much larger than could possibly be accounted for by experimental error. It is smaller, but of the same order of magnitude as that calculated by Jahn[2] using Dixon's[1] measurements, namely 5.673 cal./deg.

There seems to be no escape from the assumption that the analyses of the spectroscopic data for nitric oxide and chlorine are correct. Accordingly, the discrepancy is caused by some uncertainty in the spectroscopic data for nitrosyl chloride, or its energy levels are degenerate as a result of some unknown factor. The former possibility only can be considered here. The discrepancy is such that the entropy of nitrosyl chloride calculated from spectroscopic data is too small. Consideration must be given to factors that would increase it by $\frac{1}{2}$ 3.6=1.8 E.U.

The interatomic distances of Ketelaar and Palmer cannot be increased greatly without making them improbably large. The Cl−N distance of 1.95A is, according to these authors, already larger by 0.26A than that to be expected. A change in the bond angle from 116° to the improbably small value of 90° increases S°_{NOCl} by only 0.3 E.U. Accordingly it does not seem likely that the discrepancy results from uncertainty in the size or shape of the molecule.

It is possible that not all of the frequencies reported by Bailey and Cassie are fundamentals. The frequency 1832 cm^{-1} is, as is to be expected, nearly equal to that found with nitric oxide, 1888 cm^{-1}, and hence is, in all probability, a fundamental. The following considerations indicate that the 923 cm^{-1} frequency is not a fundamental. Lechner[20] has derived formulas for the fundamental frequencies of unsymmetrical triatomic molecules as a function of the force constants for stretching and bending. The force constants for the N=O and N−Cl bonds may be evaluated from Badger's Rule[21] and were found to be $k_{12}=15.0\times10^5$ and $k_{23}=1.6\times10^5$ dynes/cm, respectively. Two of Lechner's relations take the following forms:

$$\omega_1^2+\omega_2^2+\omega_3^2=35.92\times10^5+6.01d, \quad (19)$$

$$\omega_1^2\omega_2^2\omega_3^2=346\times10^{10}d, \quad (20)$$

where d is the bending force constant and ω_1, ω_2, ω_3 are frequencies expressed in cm^{-1}. If the molecule were linear the terms ω_2^2 and $6.01d$ in the first equation would be absent. With $\omega_1=1832$ cm^{-1}, ω_3 becomes 490 cm^{-1}. The molecule is not linear but has a bond angle of 116°. The value of ω_3 will be somewhat different for the bent model but not greatly so; it seems reasonable then to select the observed frequency 633 cm^{-1} for ω_3. It is now possible to evaluate approximately the bending frequency ω_2 and the force constant d. ω_2(calc.)=346 cm^{-1}. $d=0.46\times10^5$ dyne/cm. This value of ω_2 is considerably lower than the lowest observed frequencies, namely 633 cm^{-1} and 923 cm^{-1}. If it is assumed that the greater of these is a combination such that 923 =633+290, then the fundamental frequencies for nitrosyl chloride become 1832, 290 and 633 cm^{-1}, respectively. Professor R. M. Badger has called our attention to the fact that further support for the assumption is provided by the low

[20] Lechner, Monatshefte für Chem. **61**, 385 (1932).
[21] Badger, J. Chem. Phys. **2**, 128 (1934); **3**, 710 (1935).

bending frequency[22] of 397 cm^{-1} for $Cl-C\equiv N$, a linear molecule that is probably stiffer than $Cl-N=O$. The assumption of the low bending frequency leads to a much smaller discrepancy between theory and experiment, namely

$$\Delta S°(\text{spect.})-\Delta S(\text{expt.})=0.40 \text{ E.U. at } 100°$$
$$=0.10 \text{ E.U. at } 220°$$

and the largest of these values is only slightly greater than the average experimental error, ±0.3 E.U. The effect of the lowered frequency on ΔC_P has been taken into account, and the effect on $\Delta H°$ and $\Delta F°$ is found to be less than the experimental error.

Another possible interpretation of the infra-red spectrum is that both the 923 cm^{-1} and 633 cm^{-1} bands are first harmonics. The fundamentals would then be 1832, 317 and 462 cm^{-1}, respectively. This interpretation would be in accord with the considerations based on Lechner's formulas. The discrepancy between the spectroscopic and experimental entropy changes is reduced to 0.30 cal./deg. at 220° and to 0.80 cal./deg. at 100°. This result is not as satisfactory as that obtained through the assumption that $923=633+290$ cm^{-1}.

The discrepancy reported by Jahn is to a large extent removed if the assumption of the lowered frequency is made. That it is not wholly removed may possibly be ascribed to the experimental errors in Dixon's results.

The possibility of finding some new and interesting kind of degeneracy should not, of course, be overlooked. Before ascribing the discrepancy to such a cause a further investigation of the infra-red spectrum of nitrosyl chloride should be made, or its heat capacity determined. Because of the intense red color of the substance it has not been found possible to obtain its Raman spectrum.[23] The tentatively predicted frequency of about 290 cm^{-1} falls in the infra-red region at 30–40μ.

[22] Sutherland, Proc. Roy. Soc. **A156**, 654 (1936).

[23] Dadieu and Kohlrausch, Physik. Zeits. **33**, 165 (1932).

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On the Viscosity of Nonpolar Liquids

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The phenomenon of viscosity drop by flow-orientation (i.e., mechanical orientation in a Couette apparatus) with nonpolar liquids composed of large dissymmetrical molecules points to a marked influence of the dissymmetry of polarizability on this phenomenon and on viscosity in general. In the case of such liquids the molecular forces of interaction are practically confined to the dispersion forces, and there are very definite states of minimum mutual potential energy. This condition results in temporary formation of complexes of higher saturation of those residual fields of force which interact in the phenomenon of viscosity. An analogous case is represented by long chain hydrocarbon molecules with polar head where the dipole forces are eliminated to a great extent, insofar as viscosity is concerned, by association, resulting in a viscosity behavior very similar to that of corresponding paraffins. With small molecules, even small permanent moments tend to suppress the influence of the anisotropy of polarizability of deformation, resulting in a type of complex which is ultimately, even temporarily, more determined by the dipole forces.

THE present attempt of examining the factors which determine the viscosity of nonpolar liquids has its origin in an engineering problem treated some years ago, relating to the theory of lubrication.

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Starting with the fundamental equation of Newton, (1) $F=\eta_T \cdot A \cdot \partial u/\partial h$ in which F is the frictional force, A an area (the lubricated area), η_T the absolute viscosity and $\partial u/\partial h$ the gradient of shear between two lubricated faces of a bearing of infinite length in motion, Osborne Reynolds

and A. Sommerfeld developed the hydrodynamic theory of lubrication. It follows from this theory that the frictional work should, so far as the lubricant is concerned, depend exclusively on the viscosity at the operating temperature.

The theory has been frequently tested experimentally by engineers by measuring the torque of model bearings. With due allowance for the different boundary conditions of theory and experiment, a marked discrepancy was found in some cases (too low torques), and speculation as to the reasons started.

Because of the fact that discrepancies were greatest with certain electrically polymerized oils which contain molecules of extraordinarily high molecular weight, the explanation appeared plausible that these molecules are orientated by the flow in its direction and show a smaller viscosity in that state of order. This hypothesis[1] was confirmed by viscosity measurements in a modified Couette apparatus, essentially designed by L. Prandtl for the purpose.[2]

The apparatus (Fig. 1) consists of two cones, the inner of which is rotated. The rotating journal contains a bore through which oil is supplied under slight pressure which determines the film thickness or clearance h, which is read at a gauge on top. The torque at the outer cone is balanced and then measured by weights. The outer cone is protected by a felt cover and the temperature measured at the outer cone after a stationary state is reached. It can be shown in three ways that the effect is *not* a temperature effect. The simplest proof lies in the fact that one measured point u/h may be obtained by an infinity of variations in u and h: On varying these values, temperatures are measured which vary from 20°C to 50°C, resulting in varying heat transfer. On reducing them to 20° as in Fig. 2, they all fall on the same curve.

Writing Newton's equation in the form, (2) $P/(u/h)=(A\cdot r/a)\eta_T$* the term in brackets is a constant of the apparatus and $P/(u/h)=$constant, unless $P/(u/h)=f(u/h)$. Fig. 2 shows this function, slightly transformed, expressing the angular speed in r.p.m. for various oils. The decrease in viscosity, $\Delta\eta$, for various oils depends both on viscosimetric viscosity *and* on the *type* of oil. The dependency of the *temperature* coefficient of viscosity on the type of oil is well known.

As would be expected, $\Delta\eta$ is largest with the oils which contain the longest molecules, e.g., the polymerized oils. It appears desirable to find

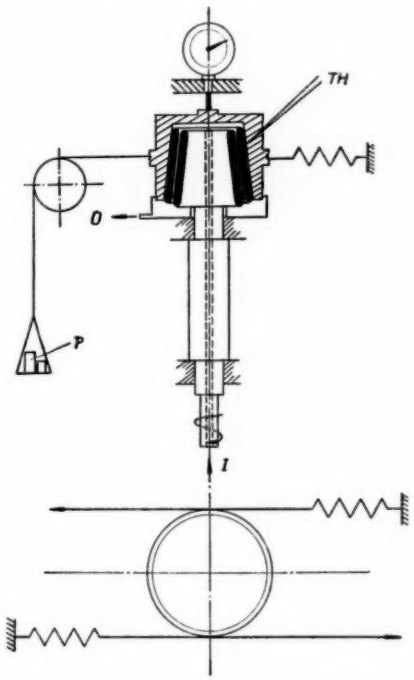


FIG. 1. Oil testing apparatus of Prandtl. TH = thermocouple, O = oil outlet, and I = oil inlet.

a correlation between this and any viscosity behavior and the molecular structure of liquids.

The only thing we know for certain of these highly heterogeneous oils is that some are composed mostly of the isomers of paraffins, i.e., chain compounds, while in others nuclear structures like cyclopentane- and cyclohexane-nuclei forms are essential parts of the structure. The chain molecules have a smaller temperature coefficient of viscosity than the nuclear structures.

Our knowledge of the liquid state and the intermolecular forces has been extended so far these last years, that it appears possible to approach the viscosity problem from a structural point of view, at least to such an extent as to

[1] S. Kyropoulos, Physik. Zeits. **29**, 942 (1928).
[2] S. Kyropoulos, Forschung Ingenieurwes. **3**, 287 (1932).
* See S. Kyropoulos, Forschung Ingenieurwes. **3**, 287, 290 (1932), for detailed explanation. $F=P\cdot a/r_m$, where P is a weight, a the lever arm, r_m the mean radius of the inner cone Fig. 1, A the effective area and h the clearance between the cones.

find its various determining factors in simpler cases and to find, thus, what experimental data may lead to its better understanding.

The effective forces are:

(1) The orientation effect of dipoles or multipoles, temperature-dependent, because it is disturbed by heat motion;

(2) The induction effect of dipoles (or, much smaller, multipoles) on neighboring molecules, independent of temperature as a polarization of deformation.

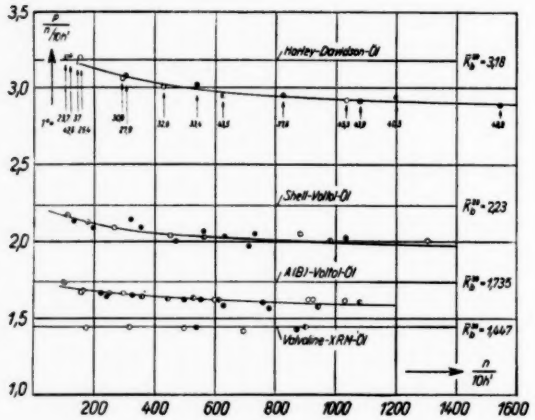


FIG. 2. Decrease of viscosity (ordinates) with increasing gradient of shear (abscissae). (Reproduced from S. Kyropoulos, Forschung Ingenieurwes. **3**, 287 (1932)). $n/10h'$ is proportional to u/h, the speed u being transformed into revolutions per minute, the cm clearance h into mm as measured in the experiments.

The magnitude of these effects depends not only on the magnitude of the moment and the polarizability, but also on the *location of the moment* within the molecule, its accessibility. In more extended molecules we have to expect largely independent effects of the individual *group* moments of which the whole moment is constituted. The inaccessibility of the moment by attached groups shielding it may go so far that dipole association is entirely absent, as in ether, which does not mean absence of aggregate (or "*group*") formation in the liquid.† This latter is, however, brought about by the third type of forces, *viz:*

(3) The dispersion effect: A result of the short period electron motion, dependent on the polarizability and independent of temperature.

An examination of viscosity from the point of view of molecular forces amounts to a discussion of association in the liquid state. We will first consider the case of hydrocarbons, where the main forces are the dispersion forces.

Association between two molecules results in a state of order of lower potential energy compared with the state of disorderly independence. It will be the stronger the more atoms of the molecule take part and the stronger the individual fields of force are. Furthermore, there will be stronger association as the number of positions of closest approach increases, e.g. with planar or highly symmetrical structures. The individual force fields will be largest where the polarizability is largest. Thus, with straight chains, an arrangement end to end means attraction at the strongest fields of force, because it is this direction in which the *maximum* polarizability α_{max} lies. Nevertheless, this is not the position of minimum potential energy of two molecules, because there are only two points "in contact" whereas we get the greatest contact area when the molecules are arranged side by side. A *group* of molecules with this arrangement has its strongest fields at the ends of the chains because of the direction of α_{max}, and because they lie farther apart than the CH_2 groups, which results in the well-known perpendicular adsorption at solid surfaces. Thus, in the liquid, group formation will take place in two directions, and mechanical flow orientation will result in an interaction between fields of force with the smaller polarizability, perpendicular to the chains and α_{max}, i.e., in a smaller viscosity. Thus, flow orientation and the accompanying decrease of viscosity show that the molecule groups are *longer* in the direction of α_{max}, primary side-by-side association *adding* to the attracting effect of α_{max} the effect of a large area of contact in the direction of the longest axis of the molecule.

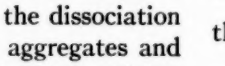
If a molecule has a more planar structure, like cyclohexane, with rotational symmetry, there

† "Aggregate" and "group" are used as synonyms to avoid confusion with the intramolecular groups of atoms to which the "group moments" refer. Both words stand for the (today better defined) concept of "Schwarm" used by Bose, Physik. Zeits. **9**, 708 (1908) in connection with crystalline liquids. Nothing is assumed as to their size. In some cases certain phenomena have been interpreted as indicating a rather definite size, e.g.: G. Antonoff, Phil. Mag. (6) **50**, 265 and (7) **1**, 1121 (1926); S. Kyropoulos, Zeits. Wiss. Photogr. **29**, 167 (1930); A. Goetz, Internat. Conf. on Physics, London 1934, II, 62, (metallic state).

are more positions of maximum attraction for the same approach of two molecules which will become the more apparent with increasing density and decreasing heat motion. This means a planar structure should result in a greater temperature coefficient of viscosity.

Stronger bonds between two molecules should result not in stronger but in weaker residual fields. The extreme case is the formation of a definite chemical compound. Thus, in the case of benzene with its six semi-free p electrons, we should expect groups of higher saturation and consequently smaller forces *between the groups*, i.e., smaller viscosity than with cyclohexane. With increasing temperature the groups of higher saturation will disintegrate into groups of lower saturation which means that the lowering effect on viscosity of temperature motion is balanced to a certain extent by the dissociation of the groups into such smaller aggregates and into individual molecules with their higher anisotropy and higher polarizability.

Association or group formation results in the formation of molecular complexes of lower mutual potential energy, lower anisotropy of polarizability and, in the case of dipoles, more shielded polar groups, or even in the formation of groupings of higher symmetry, quadrupoles, etc., with a much shorter range of action. All these phenomena are in the direction of lowering the residual forces, i.e., viscosity. We might express it by saying that the reversal of association makes the associating forces more available for viscosity or that bonds of longer time of lingering are transformed into bonds of shorter duration. The stronger the association is, the smaller will be, relatively speaking, the viscosity at a given temperature and the smaller the temperature coefficient of viscosity, i.e., the induction effect and the temperature dependent orientation effect act with increasing temperature in a direction which one would not expect, notably with the latter effect, on disregarding association and dissociation.

This effect which is in the case of benzene caused by molecular anisotropy and its nonlocalized electrons is modified in toluene and in the xylenes by the dipole effect. If we assume in accord with other evidence[3] that it is the *partial* moments of a polar molecule which become effective in dipole association, and that groups of the resulting double etc. molecules are held together rather by dispersion forces and less by the shielded permanent moments,[4] then we should expect with toluene a double molecule of the type  as the unit of the group.* Further association is most stable when the double molecules are packed with maximum contact surface, i.e., close with their benzene

[3] G. Briegleb, Zeits. f. physik. Chemie (*B*) **16**, 249, 270 (1932).

[4] G. Briegleb, Zeits. f. physik. Chemie (*B*) **10**, 205 (1930).

* This type of dipole association is assumed already by Briegleb, Zeits. f. physik. Chemie (*B*) **16**, 270–272, on discussing association (not *group* formation). H. A. Stuart and H. Volkmann, Zeits. f. Physik **83**, 461, 475, (1933) reject that conception, considering a benzene-type layer-association with the p electrons. In our conception we discriminate with polar molecules with exposed moments between "primary" association = dipole association and "secondary" association or group formation. The first step corresponds to Briegleb's conclusion, the second to Stuart's. Both steps are discussed with relation to pure association phenomena by Briegleb in reference 4 for the particularly illustrative case of the fatty acids. Considering the *partial* moments of the molecules as effective in association means strict analogy with orientation on surfaces and adsorption (see F. V. Lenel, Zeits. f. physik. Chemie (*B*) **23**, 379 (1933).

TABLE I.* *Isomeric heptanes.*

No.		b.p. C°	η(b.p. ×0.789)*	d*	P_{TOTAL}	A	C
1	*n*-heptane	98.4	0.00409	0.6737	34.65	1	—
2	3·ethylpentane	93.3	412	7018	.24	2	p.s.
3	3·methylhexane	91.8	407	6912	.49	2	—
4	2·methylhexane	90.0	416	6845	.70	2	—
5	2·3 dimethylpentane	89.7	444	7007	.42	2	i.
6	3·3 dimethylpentane	86.0	497	7015	.45	<2	p.s.
7	2·2·3 trimethylbutane	80.9	—	7013	.38	<6	i.
8	2·4·dimethylpentane	80.8	411	6861	.75	<5	—
9	2·2·dimethylpentane	78.9	438	6867	.73	<8	—

* b.p. = boiling point C°, η(b.p. ×0.789)* = absolute viscosities at corresponding temperatures, corresponding to $\eta 20°$ for *n*-heptane, d* = densities for the same corresponding temperatures, P_{total} = total molar polarization ($P_E + P_A$), A = estimated optical anisotropy, C = configuration characteristics, p.s. = planar symmetry, *i.* = strong intramolecular polarization, $(b_1 - b_2) \times 10^{-25}$ = optical anisotropy, μ = dipole moment (total) in D units.

TABLE II.* *Viscosities of substances at corresponding temperatures 0.798×b.p. and 0.975×b.p.*

n-HEXANE b.p. 69°	*n*-HEPTANE b.p. 98.4°	*n*-OCTANE b.p. 124.6°	ISOHEPTANE b.p. ~92°
$\eta 0$: 0.004012 $\eta 60$: 0.002288 $\Delta\eta/\Delta t \times 10^4$ 0.2875	$\eta 23$: 0.004040 $\eta 89$: 0.002256 : 0.270	$\eta 45$: 0.004117 $\eta 115$: 0.002248 0.267	$\eta 18.5$: 0.003915 $\eta 83$: 0.002195 : 0.267
CCl_4 b.p. 76.75°	$CHCl_3$ b.p. 61.2° $\mu = 1.15$	Cyclohexane b.p. 80.8°	Benzene b.p. 80.5°
$\eta 6.2$: 0.012191 $\eta 68$: 0.005459 $(\Delta\eta/\Delta t) \times 10^4$: 1.09	$\eta - 6.2$: 0.007516 $\eta 53$: 0.004245 : 0.699	$\eta 15$: 0.01056 $\eta 60$:0.00534 : 1.16 $(b_1 - b_2) \cdot 10^{25} = 30$	$\eta 10 = 0.007631$ $\eta 60$: 0.003980 0.731 59.6
Toluene b.p. 110.3°	*o*-xylene b.p. 144°	*m*-xylene b.p. 139°	*p*-xylene 136.2°
$\mu = 0.4$ $\eta 33.5$: 0.005061 $\eta 110$: 0.002588 $(\Delta\eta/\Delta t) \times 10^4$: 0.323 $(b_1 - b_2) 10^{25}$: 81.6	$\mu = 0.5$ $\eta 10$ 0.009368 $\eta 80$ 0.004168 0.743 97.6	$\mu = 0.4$ $\eta 10$: 0.007019 $\eta 80$: 0.003455 0.509 76.1	$\mu = 0$ $\eta 10$: 0.006475 $\eta 80$: 0.003519 0.422 94

* For explanation see footnote to Table I.

nuclei. We see that, by preceding dipole association, in the case of toluene, the planar symmetry of benzene and cyclohexane (nearly planar) is lost, and the elementary double molecule has, insofar, more the characteristics of a paraffin hydrocarbon with lower viscosity at corresponding temperatures, because there are fewer positions of minimum potential energy. In accordance with the presence and easy accessibility of the polar group of the *individual* molecule, the temperature coefficient of viscosity is smaller than with the nonpolar benzene. Moreover, the various side-by-side positions with two or more toluene monomolecules are probably less different in energy than with double molecules; i.e., the monomolecules are more benzene-like, an effect in favor of high viscosity.

In the series of the xylenes the total dipole moment drops from 0.5–0.4–0 in the order *o-m-p*. Considering the partial moments and the effect of their distance in the molecule, which includes both intramolecular polarization and accessibility, we have to expect dipole association in the order *p-m-o*. The *p* compound should be most toluene-like and remotest from planar symmetry, the *o* and *m* compounds more benzene-like, notably the *o* compound where dipole association is least because of the disturbing effect of intramolecular polarization. The two polar groups act more like a unity, whereas in the *m* and *p* molecules there are *two* groups with stronger attractive forces. Both the absolute magnitudes and the temperature coefficients of the viscosities are in accord with these structural characteristics. The associating effect of the dipoles dominates in this group over the effect of molecular anisotropy.

Table I shows some data[5,6] referring to the isomeric heptanes. Viscosities and densities are reduced to corresponding temperatures, corresponding to 20°C for *n*-heptane. The viscosity value for 2·2·3·trimethyl butane has been omitted because the value for η_{20} in the original paper (0.00585 against 0.00454 as the highest of the rest of the series) appears doubtful. "*A*" is the molecular anisotropy roughly estimated by applying the rule of Silberstein[7] in decreasing order, the figures meaning the order in which the isomers appear in the table (first column). The isomers are tabulated in the order of decreasing boiling point. This order appears to coincide with the order of decreasing anisotropy within the limits of accuracy of its rough estimate. The last column "*C*" contains remarks on the atomic configuration, p.s. = planar symmetry; *i* = strong intramolecular polarization. The molecular forces of some of the isomers should be sufficiently different to show slight differences in the temperature coefficient of viscosity, whereas the approximation to planar structures is, of

[5] G. Edgar and G. Calingaert, J. Am. Chem. Soc. **51**, 1540 (1929).
[6] C. P. Smyth and W. N. Stoops, J. Am. Chem. Soc. **50**, 1883 (1928).
[7] L. Silberstein, Phil. Mag. (6) **33**, 92, 215, 521 (1917).

course, slight in comparison even with cyclohexane, meaning with certain heptane isomers rather an increased chance of closest approach in various directions.

The effect of dipole association on "group saturation" and on the temperature coefficient (dipole *dis*sociation) is shown by comparing CCl_4 and $CHCl_3$ at corresponding temperatures (Table II). A similar effect is exhibited by proceeding from cyclohexane to benzene. Comparing these with the former pair, however, the practical identity of the boiling points shows that the attractive forces themselves do not depend on temperature in the case of benzene as the dipole forces do with chloroform. The viscosity behavior of the substituted benzenes and their isomers is particularly illustrative for the possibilities of development of the method used, which takes for a starting point the group-forming properties of the molecules as represented by their potential "area of contact," their anisotropy of polarizability, their partial moments and the accessibility of these moments. It is this tendency of shielding the moments by dipole association and of decrease of anisotropy by association which tends to abandon the greatest part of the cohesion forces, *viz.* the residual forces between *groups* of molecules to polarizability forces, i.e., practically dispersion forces. It is for this reason that so many polar liquids follow so well the equation of Andrade.[8*]

[8] E. N. da C. Andrade, Phil. Mag. (7) **17**, 497, 698 (1934).

[*] An unusually interesting treatment of the viscosity problem is presented by Eyring and his co-workers in the reaction rate theory of viscosity (H. Eyring, J. Chem. Phys. **4**, 283 (1936) and R. H. Ewell and H. Eyring, J. Chem. Phys. **5**, 726 (1937); see also Ewell's article in J. App. Phys. **9**, 252 (1938)). In the author's opinion it would appear promising to incorporate the ideas of the present paper in Eyring's theory. The substitution of aggregates for individual molecules would greatly facilitate considerations of symmetry of fields of force and association with some compounds, because it is just the decrease of anisotropy (compared with the individual molecule) which characterizes the formation of molecular aggregates.

Summary

The viscosity behavior of liquids is primarily determined by the residual fields of force of the *groups* of molecules which constitute the liquids. The structural characteristics of the individual molecule—its polarizability, the anisotropy of polarizability, geometrical symmetry, intramolecular polarization, its partial permanent moments and their accessibility—determine group formation and the type and strength of association which is comparable to intramolecular polarization and determines the residual fields of force of the groups which are essentially dispersion forces. Group formation results in saturation of dipole forces and decrease of the anisotropy of the group. Group formation means the existence of loose bonds of longer duration in comparison with the "bonds" of *short* duration which constitute the measurable cohesional forces. In the case of polar molecules disintegration of larger groups into smaller ones and dipole-dissociation with rising temperature appear as a diminished rate of decrease of viscosity, with increasing temperature bonds of longer duration being transformed into additional bonds of short duration. Loosely bound electrons act in a similar way.

Hindered Molecular Rotation and the Dielectric Behavior of Condensed Phases

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The polarizability of a liquid or a collection of randomly oriented single crystals in which polar molecules are unable to move except to rotate from one to the other of two equilibrium orientations separated by an angle β and of potential energies whose difference is E, is

$$\alpha=(\mu^2/6kT)(1-\cos\beta)/\cosh^2 E/2kT,$$

where μ is dipole moment. This model accounts for the reduction of α in solids and liquids from the value $\mu^2/3kT$ observed in gases, and at the same time provides for anomalous dispersion in terms of discontinuous molecular processes.

THE effect of the internal field of a liquid in reducing the rotational polarizability of polar molecules has been calculated by P. Debye,[1] who used as the simplest approximation a potential function of the form

$$V=-(E/2)\cos\theta, \qquad (1)$$

where V is the energy of interaction of a given molecule with its neighbors, θ is the angle between the direction of the molecular dipole and the instantaneous direction of minimum potential energy, and E is the height of the potential barrier over which the molecule must pass in end-over-end rotation. This function permits rotational motion of the dipole about two axes, and yields upon calculation the polarizability

$$\alpha=(\mu^2/3kT)[1-(\coth E/2kT-2kT/E)^2]. \qquad (2)$$

Thus the magnitude of the potential barrier E should at a given temperature determine the factor by which the polarizability of a liquid is reduced from the value expected in the gaseous state. These considerations apply equally well to a solid composed of a large number of randomly oriented single crystals.

Another effect of molecular interaction is the anomalous dispersion of dielectric constant and the accompanying dielectric loss which appear in solids and liquids whose molecules engage in rotational motion.[2] F. C. Frank[3] has proposed to explain this in terms of discontinuous molecular processes by assuming that there are two or more equilibrium orientations available to the molecule, and that as a consequence the relaxation time of the rotational polarization is in the simple case a function of the magnitude of the potential barriers separating these orientations. Eq. (1) provides only one equilibrium orientation, and hence requires the introduction of the added assumption of an inner friction in order to account for the dielectric absorption.[1] It is desirable in the interest of economy to find an explanation in terms of rotation between two or more equilibrium orientations which accounts both for the dielectric absorption and for the reduction of polarizability below $\mu^2/3kT$ found in condensed phases of many polar compounds.

A simple approach to this problem is to assume that the molecule with its dipole can rotate about only one axis, and that the potential opposing this rotation is

$$V=(E/2)(1-\sin n\theta) \qquad n=2, 3, 4, \cdots,$$

giving n equally spaced equilibrium orientations of equal potential energy. The usual statistical mechanical calculation of the effect of applying a vanishingly small external field yields the static polarizability

$$\alpha=\mu^2/3kT$$

for a liquid or for a solid composed of a large number of randomly oriented single crystals.*

[1] P. Debye, Physik. Zeits. **36**, 100 (1935); Chem. Rev. **19**, 171 (1936).
[2] P. Debye, *Polar Molecules* (The Chemical Catalog Co., 1929).
[3] F. C. Frank, Trans. Faraday Soc. **32**, 1634 (1936).

* Integration of expressions containing $e^{a\sin n\theta}$ was desired in this calculation. Dr. L. A. MacColl pointed out the necessary transformation, which is

$$e^{a\sin n\theta}=\cos(ia\sin n\theta)-i\sin(ia\sin n\theta)$$
$$=J_0(ia)+2\Sigma_k J_k(ia)\cos kn\theta-2i\Sigma_l J_l(ia)\sin ln\theta,$$

where $k=2, 4, 6\cdots$, $l=1, 3, 5\cdots$, and the J's are Bessel functions of order k and l respectively.

While this assumption accounts for long relaxation times at low temperatures in terms of Frank's theory, it fails to provide for the experimentally observed reduction of the polarizability of condensed phases from the values for the corresponding gases. The most obvious defect of this potential function, particularly for polar molecules, is its assumption of equal potential energies for each of the equilibrium orientations. Another defect lies in the assumption that the equilibrium orientations are separated from each other by equal angles.

In order to take account of these factors in a readily calculable manner, the very simple assumption is made that the molecule may occupy either of two fixed orientations separated by an angle β, and may engage in no rotational motion except to move from one of these orientations to the other.* The plane of these orientations determines the xy plane of a system of Cartesian coordinates. One orientation, of potential energy E, lies along the x axis, while the potential energy of the other orientation is set equal to zero. The effect of any applied field F is then wholly determined by the components F_x and F_y in the xy plane. The mean dipole moment along the x axis is

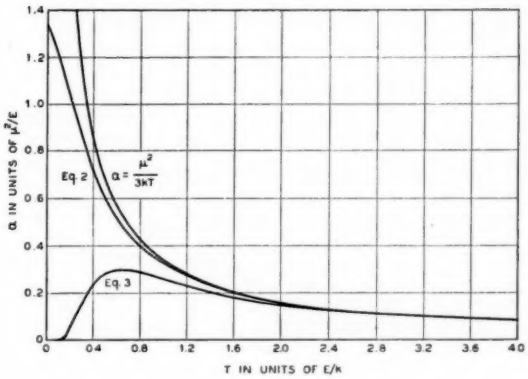

FIG. 1.

$$\bar{m}_x=\mu\frac{\exp\left(-(E-\mu F_x)/kT\right)+\cos\beta\exp\left((\mu F_x\cos\beta+\mu F_y\sin\beta)/kT\right)}{\exp\left(-(E-\mu F_x)/kT\right)+\exp\left((\mu F_x\cos\beta+\mu F_y\sin\beta)/kT\right)},$$

while

$$\bar{m}_y=\mu\sin\beta\frac{\exp\left((\mu F_y\sin\beta+\mu F_x\cos\beta)/kT\right)}{\exp\left(-(E-\mu F_x)/kT\right)+\exp\left((\mu F_y\sin\beta+\mu F_x\cos\beta)/kT\right)}.$$

Saturation effects are neglected as usual by expanding the exponentials involving the field to the second term only. Now when φ_x and φ_y are the angles between the applied field and the indicated Cartesian axes,

$$\bar{m}=\bar{m}_x\cos\varphi_x+\bar{m}_y\cos\varphi_y,$$

$$F_x=F\cos\varphi_x,$$

and

$$F_y=F\cos\varphi_y.$$

After appropriate substitutions and averaging φ_x and φ_y over a sphere, the polarizability of the liquid or collection of randomly oriented single crystals is found to be, in the direction of the field,

$$\alpha=(\mu^2/6kT)(1-\cos\beta)/\cosh^2(E/2kT). \quad (3)$$

It is easily seen that at finite temperatures Eq. (3) reaches its limiting value, $\mu^2/3kT$, only when $\beta=180°$ and $E=0$. Any other value of β or E reduces the polarizability below the value expected in gases in accord with experiment. At the same time this picture provides more than one equilibrium orientation as required by Frank's theory of anomalous dispersion, although nothing is here specified regarding the height of the potential barrier between orientations, as would be required in a calculation of the relaxation time.

The effect of the angle β in reducing the polarizability is quite simple, being independent of temperature. On the other hand the reduction of polarizability due to the difference E in the energy of the equilibrium orientations is a function of temperature, and one whose behavior is quite different from that of the reduction factor of Eq. (2). This is illustrated for $\beta=180°$

* This model is a generalized form of that originally proposed by Debye (reference 2) in considering anomalous dispersion in ice.

in Fig. 1, where the polarizability of Eq. (3), expressed in terms of μ and E, is plotted against temperature expressed in terms of k and E; Debye's Eq. (2) is plotted in terms of similar reduced coordinates, where E represents the height of the potential barrier opposing molecular rotation. The principal difference in the qualitative behavior of the two functions is that with declining temperature Eq. (3) reaches a maximum and then falls off to zero at 0°K, while Eq. (2) increases steadily to the limiting value

$$\alpha = (4/3)\mu^2/E.$$

This is because the polarizability of Eq. (2) at 0°K is that of a rotational harmonic oscillator with two degrees of freedom, while Eq. (3) is concerned only with rotational motion from one equilibrium orientation to another, excluding by assumption the contribution of any rotational harmonic oscillation about a given equilibrium orientation.

If among several equilibrium orientations there is one whose potential energy is lower than that of any of the others, the Maxwell-Boltzmann function requires that all molecules occupy this one orientation at absolute zero. It follows that, excluding saturation effects, there can be no contribution to the polarizability due to rotation from one orientation to another in such a system at 0°K. Hence the behavior of Eq. (3), showing a maximum for that part of the static polarizability which is due to rotation from one equilibrium orientation to another, is characteristic of any potential function describing two or more equilibrium orientations of which one is of lower potential energy than any of the rest. This generalization applies to that part of the polarizability of any pure non-ionizing polar liquid or solid which is subject to anomalous dispersion, if the anomalous dispersion is due to the existence of potential barriers between equilibrium orientations.

The great length of the relaxation times expected at very low temperatures will in general prevent experimental observation of the maximum of polarizability predicted by Eq. (3), because of the impossibly long charging times that would be required to observe the true static dielectric constant. Only a favorable combination of relatively low potential barrier with large difference in the energy of equilibrium orientations could be expected to produce this maximum under observable conditions. The rapid rise of dielectric constant which accompanies polymorphic transitions in many crystals cannot be said to be experimental confirmation of Eq. (3), because the latter assumes the inner field to be independent of temperature, which is almost certainly not the case through the temperature range of a polymorphic transition.

Equation (3) and the assumptions on which it is based are significant, however, in presenting a crude picture which accounts for both anomalous dispersion and the observed reduction of polarizability in condensed phases; in terms of this picture the reduction factor depends not on the height of potential barriers separating equilibrium orientations but on the difference between the energies of the orientations themselves, and on the angles by which the orientations are separated.

The author is indebted to Dr. S. O. Morgan and Dr. L. A. MacColl, both of the Bell Telephone Laboratories, for helpful suggestions in connection with this work.

On the Magnetic Behavior of Vanadium, Titanium and Chrome Alum

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As Siegert has shown, the fact that the susceptibilities of both titanium and vanadium alum conform to the "spin-only" formula demands that the ratio of the fourth- to the second-order part of the noncubic portion of the crystalline potential have a certain critical value. The present paper investigates whether such a ratio can result from (I) the direct effect of the "distant" charges, i.e., the atoms more remote than the six waters immediately surrounding the paramagnetic ion, (II) the indirect action of the remote atoms in distorting or polarizing the water cluster so that it is no longer octohedral, or (III) the Jahn-Teller effect, whereby the degeneracy of the cation has repercussions on the arrangement of the surrounding waters, so that they are not cubically grouped. It is concluded that (I) does not yield a sufficiently large splitting. That the mechanism (III) cannot alone be effective is shown by Gorter's relaxation experiments, as well as by the existence of a small splitting of the basic quartet of chrome alum which cannot be due to (III), but which is revealed by adiabatic demagnetization experiments. On the other hand, (II) does give a ratio of fourth- to second-order terms of the proper size and sign, and the corresponding departures from octohedral symmetry in the water cluster need not be large enough to contradict x-ray data. The total splitting is materially amplified by the superposition of (III) on (II). It is gratifying that a model can be found which will thus yield the rather peculiar type of crystalline potential required if the basic orbital states of titanium and vanadium are both nondegenerate, but trigonal, as shown by the susceptibility data. Furthermore, it is shown in Section IV that the model gives a splitting in chrome alum of the order of magnitude 10^{-1} cm^{-1} and sign deduced by Hebb and Purcell from the magnetization at low temperatures.

THE alums are particularly suitable materials for magnetic studies, as they are magnetically dilute, they belong to the cubic system, and the detailed arrangement of the atoms is known from x-ray analysis. The purpose of the present article is to interpret theoretically certain facts connected with the susceptibilities of the vanadium, titanium and chromium alums, which previously seemed mutually irreconcilable. The susceptibilities of these three salts all conform approximately at room temperatures, and except for vanadium, also, even at liquid helium temperatures, to the "spin-only" formula

$$\chi = 4NS(S+1)\beta^2/3kT, \qquad (1)$$

where S is the spin quantum number and β is the Bohr magneton $he/4\pi mc$. The validity of (1) is well known to require that the crystalline field be such that a nondegenerate level be the normal ground state. A cubic field of a sign corresponding to six waters of coordination, as in the alums, can be shown to suffice for this purpose in chromium.[1,2] In vanadium and titanium, on the other hand, a cubic field will not lift the degeneracy of the ground level. However, x-ray analysis shows that the field surrounding the paramagnetic ion in the alums has only trigonal symmetry.[3] This is not incompatible with the cubic crystalline classification, as the microscopic symmetry of the local field need not be as great as the macroscopic symmetry. The trigonal axis coincides with one of the four body diagonals of the unit cube; one-fourth of the paramagnetic ions correspond to selection of a particular body diagonal.

The most general crystalline potential can, of course, be developed in surface harmonics

$$V = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} f_{lm}(r) P_l^m(\mu) e^{im\varphi}. \quad (\mu = \cos\theta). \qquad (2)$$

Since in the iron group we deal only with d electrons, no terms beyond $l=4$ need be included in this development, as the matrix element $\int \psi'^* \psi'' P_l^m(\mu) e^{im\varphi} d\mu d\varphi$ vanishes[4] if ψ', ψ'' are d wave functions and $l>4$. As long as there is trigonal symmetry, and also inversion symmetry

[1] Concerning the general role of nearly cubic fields in connection with the susceptibilities of paramagnetic salts, see J. H. Van Vleck, Phys. Rev. **41**, 208 (1932); R. Schlapp and W. G. Penney, *ibid.* **42**, 666 (1932).

[2] A. Siegert, Physica **3**, 85 (1936).

[3] H. Lipson and C. A. Beevers, Proc. Roy. Soc. **148**, 664 (1935); H. Lipson, *ibid.* **151**, 347 (1935).

[4] The group theory basis for this statement is that d wave functions transform like the representation D_2 of the rotation group, and the direct product $D_2 \times D_2$ involves no representations higher than $l=4$.

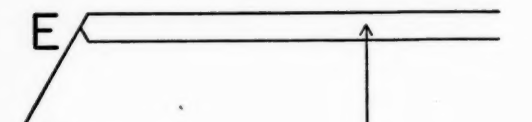

FIG. 1. The splitting of a triply degenerate cubic state in a trigonal field. The two components of E coincide, unless magnetic forces are applied.

as indicated by the x-ray data, the most general potential is[5]

$$V=f(r)+V_1+V_2, \tag{3}$$

where

$$V_1=F_1(r)[P_4^3(\mu)\cos 3\varphi-21\sqrt{2}P_4^0(\mu)], \tag{4}$$

$$V_2=F_2(r)P_2^0(\mu)+F_4(r)P_4^0(\mu). \tag{5}$$

Here $\theta=0$ is the trigonal axis, also one of the cube body diagonals. The term V_1 has cubic symmetry, and, except for a proportionality factor, is the same as $(x^4+y^4+z^4-3r^4/5)$, where x, y, z are Cartesian coordinates referred to the main cubic axes. The expression V_2 is essentially a correction for the departures from cubic symmetry, and has trigonal symmetry about a body diagonal. If we neglect the tendency of the d wave functions to overlap the charge distribution of adjacent atoms or ions, then V must satisfy Laplace's equation, and F_2, F_4 assume the form Gr^2 and $9Hr^4$, respectively, with the proportionality constants G and H independent of r. The factor 9 in the definition of H is included merely for typographical convenience. Then (5) may be written

$$V_2=(G+30Hr^2)(xy+yz+zx) -35H(x^3y+xy^3+x^3z+xz^3+y^3z+yz^3)+C, \tag{6}$$

where the additive term C has cubic symmetry, and may be omitted for our purposes.

Siegert has shown that if either the coefficient F_2 or F_4 vanishes in (5), then it is impossible for a nondegenerate level to be the basic state both in titanium and vanadium as demanded by Eq. (1). Instead there is an inversion of the Stark pattern in going from a one-electron (Ti^{+++}) to a two-electron (V^{+++}) system, so that the energy level scheme shown in Fig. 1 should be turned upside down in one case or the other. Siegert notes that only for a very special range of values of the ratio F_2/F_4 will the nondegenerate orbital state be deepest both in Ti^{+++} and V^{+++}. It is not merely necessary that the theory explain the susceptibilities of the Ti and V salts, for, as we shall see, certain additional demands upon the crystalline potential are imposed by the magnetic behavior of chromium alum at very low temperatures.

It may be taken for granted that the crystalline field comes mainly from the surrounding water molecules and is of dominantly cubic symmetry. We are, however, concerned with the deviations from the latter. They can result from three distinct causes, as follows:

I. The direct effect of the field from distant atoms. By the term "distant atoms," we mean atoms other than those contained in the six water molecules of coordination about the paramagnetic ion. Of course these waters are so near that they give by far the largest force, but since x-ray evidence, for one thing, shows that the waters are arranged in a very nearly octohedral fashion, it is quite conceivable that the noncubic part of the field comes mainly from the distant atoms, which are known to be distributed with only trigonal symmetry.

II. The indirect action of the field from distant atoms. Because of the disturbing influence of the distant atoms, the water cluster may be somewhat disturbed from its normal octohedral arrangement, and so exert a noncubic field on the central paramagnetic ion. Because the waters are so near, the disturbances need not be very large, and still may affect this ion more strongly than the direct field from the distant atoms. The water cluster then serves as a sort of middleman in making the magnetic ion feel the influence of the noncubic arrangement of the remote atoms. To be sure, one recollects that the field which a given charge a exerts directly on another charge c is usually more important than the changes in the field on c which arise because the force from a moves another charge b, and so alters the field which b exerts on c. However, in the crystal, the nearest atoms usually "touch" each other, i.e.,

[5] Cf. Siegert, reference 2. In writing Eqs. (4) and (5) we use Legendre functions normalized in the classical way, while Siegert employs functions normalized to unity.

have their atomic radii overlap, or nearly so, and so the situation is quite different from that envisaged by treating the atoms as point charges. Instead the behavior may be likened a little to that of three billiard balls, in a row, where the water molecule plays the role of the middle ball. It is thus not unreasonable that the indirect effects of the distant atoms may be the most important ones.[6]

III. The Jahn-Teller effect. A rather remarkable theorem of Jahn and Teller[7] shows that the most stable arrangement of a polyatomic molecule is always sufficiently unsymmetrical to lift any orbital degeneracy which is present. Of course a crystal is not a molecule, but for qualitative purposes it will suffice to regard the cluster $X \cdot 6H_2O$ (X=Ti, V, Cr) as a molecule embedded in a trigonal field of force. The details of the mathematics, which involve a certain amount of group and normal-coordinate theory, are reserved for the following paper.

Because of the Jahn-Teller effect, the $6H_2O$ molecules will always arrange themselves around the paramagnetic ion in such a way that the latter is in a nondegenerate state if there is stability. Consequently, if a cubic field yields a degenerate state for the central ion, the water cluster will warp itself, even without disturbing influences from distant atoms, so that it is no longer octohedrally arranged. This effect thus automatically insures that the g factor of the ground states, and of discrete excited states, always be approximately two. Stated in other words, the essence of the Jahn-Teller mechanism is that the potential or incipient degeneracy of the central paramagnetic ion has repercussions on the arrangement of the surrounding molecules. This back action is by no means negligible from an energetic standpoint, as it is of the first rather than second order in the displacement coordinates. The linear terms naturally are ultimately eliminated to achieve stability, but at the expense of lowering the symmetry, so that the spin-only formula for the susceptibility will always apply. There is no change in the position of the central paramagnetic ion, for the kinds of displacement which lift the orbital degeneracy in virtue of the Jahn-Teller effect are all of the symmetrical or even type. A displacement of the paramagnetic ion one way or the other corresponds to an uneven or odd vibration. Thus to bring out the Jahn-Teller removal of degeneracy, it does not suffice to treat the motion of a single paramagnetic ion in a crystalline field, but rather we must consider the seven-body problem $X \cdot 6H_2O$ in such a field.

In virtue of the above, it may seem as though the rare earth salts should also exhibit g factors of approximately two, contrary to experiment. However, in the rare earths, the crystalline potential is only of the order 10^2 cm^{-1}, or about 1/100 as large as in the iron group. The shift or splitting in energy due to the J−T effect varies as the square of the potential (cf. e.g., Eq. (28) of the following paper), and so only has the negligible value 10^{-2} cm^{-1} for rare earths, as compared with 10^{+2} cm^{-1} for the iron group. The corresponding displacement in position of the water molecules varies as the first power of the crystalline potential. It amounts to only 10^{-11} cm for the rare earths, instead of being about 10^{-9} as for the iron group, and is thus so very small as to be wiped out by the zero point energy, whose amplitude of vibration is of the order 10^{-9} cm^{-1}. Consequently the J-T effect is only of academic interest in the rare earths, though it often has a profound bearing on the susceptibilities of salts of the iron group.

It is our aim to try and evaluate the relative importance of the three different factors I, II, III responsible for the noncubic character of the local field, and see which plays the dominant role in connection with magnetic phenomena. These three mechanisms we will now consider in

[6] Additional evidence that the indirect effect can sometimes be more important than the direct is furnished by as yet unpublished adiabatic demagnetization experiments made by Simon, Kurti and Squire on dilute ferric alum, of which they have kindly informed the author. They find that the dilution, which is brought about by substituting aluminum for iron atoms, sometimes increases the Stark splitting. The change in the direct fields on dilution is negligible, since the aluminum and iron atoms have the same charge +3 and since their radii are negligible compared with the distance between trivalent ions. The only appreciable alteration can hence only be in the indirect field, which is possible because dilution doubtless warps and distorts the crystal structure somewhat. The theory developed in the following paper shows that the Stark splitting responds linearly, rather than quadratically, to any small changes in the positions of the nearby waters, and in our opinion it is only because of this linearity that Simon, Kurti and Squire found appreciable changes in Stark splittings on dilution.

[7] H. A. Jahn and E. Teller, Proc. Roy. Soc. **161**, 220 (1937); H. A. Jahn, *ibid.* **164**, 117 (1937).

order. It turns out that a II is probably instrumental in determining the positions of the energy levels, but that is considerably modified by the superposition of III.

I. Direct Effect of the Distant Atoms

The simplest way of obtaining a noncubic field is merely to compute the Coulomb field exerted by the distant atoms, treated as point charges e_i. If their potentials be expanded as a power series in ascending powers of x, y, z, then it can be shown that the coefficients G and H in (6) have the following values

$$G=-\Sigma_i e_i e R_i^{-3}(\tfrac{3}{2}\cos^2\alpha_i-\tfrac{1}{2}), \tag{7}$$

$$9H=-\tfrac{1}{8}\Sigma_i e_i e R_i^{-5}[35\cos^4\alpha_i-30\cos^2\alpha_i +3+7\sqrt{2}\cos\alpha_i\sin^3\alpha_i\cos(\beta_i-\beta_0)]. \tag{8}$$

Here R_i, α_i, β_i are polar coordinates specifying charge i relative to the paramagnetic ion, with the axis $\alpha=0$ that of trigonal symmetry. The apse angle β_0 is to be so determined that

$$\Sigma e_i R_i^{-5}\cos\alpha_i\sin^3\alpha_i\sin 3(\beta_i-\beta_0)=0. \tag{9}$$

This condition has two solutions for β_0, differing by 60°; the solution is to be used which makes the total field most nearly cubic. As most of the cubic field is from the nearby water molecules, not much harm will be done if the cubic axes of reference are taken to be the same as the principal axes of the water octohedron; hence without appreciable error, the apsoidal plane $\beta_0=0$ may be identified with a plane containing the trigonal axis and some H_2O molecule located in the upper hemisphere $\alpha<\pi/2$. The results (7) and (8) are obtained by transforming in the usual way all the spherical harmonics in the expansion of the potential so that they are referred to the trigonal axis, and noting that a potential of the form (4) is of trigonal symmetry, and may be subtracted out.

As the positions of the distant atoms are known from the useful x-ray measurements by Lipson and Beevers,[3] this procedure seems at first sight rather straightforward. However, the difficulty is that it is impossible to tell how much charge is to be identified with a given atom. In fact, the electrons surely cannot be localized on one atom, inasmuch as nearest atoms in the crystal are in contact. Thus the electrons in the SO_4 group, for instance, continually wander from atom to atom. Generally speaking, one should expect the noncubic fourth-order field from the distant atoms to be of the order r^2/R_i^2 times as large as the second-order field, where r is the radius of the d shell. If this is the case, the fourth-order potential is subordinate in importance to the second-order part, whereas the empirical position of the energy levels demands that the noncubic second- and fourth-order terms be roughly coordinate in importance. However, for particular, rather exceptional atomic arrangements the second-order part of the field, from different groups of remote atoms, largely cancels, accentuating the fourth-order portion.

The most important forces, apart from those exerted by the immediately surrounding water cluster, doubtless come from the 32 oxygen atoms and 8 sulphurs in the eight nearest SO_4 groups. We therefore shall compute the "distant" part of the potential on the assumption that it comes from these 40 atoms alone. They are, unfortunately, not the only atoms inside a unit cell containing our given unit $X\cdot 6H_2O$ at the center. There are also 42 H_2O molecules, not to be confused with the six waters of immediate coordination. It would be hard to allow quantitatively for their fields, as it is not known how their dipole moments are oriented in space. Their effect is probably not especially important, as they are not so near the paramagnetic ion as are the nearest oxygens, and as they are not so highly charged as the latter. Even the nearest oxygen is over twice as far away as the waters of coordination. The walls of the unit cube contain 12 V^{+++} (or Ti^{+++} or Cr^{+++}) and 14 NH_4^+ (or K^+) ions.[8] They yield a strictly cubic field, but

[8] The parameters specifying the positions of the individual atoms are listed by Lipson and so need not be documented here. Unfortunately they do not give detailed values for $NH_4V(SO_4)_2 12H_2O$ and $KCr(SO_4)_2 12H_2O$, the salts employed in the magnetic measurements. However, he states that the ammonium alums have the "α-structure," like the potassium or rubidium ones, and the alum structure is apparently not sensitive to the trivalent ion employed, i.e., whether it is V, Cr, etc., instead of Al. So we use the parameters given for $RbAl(SO_4)_2 12H_2O$ or $KAl(SO_4)_2 12H_2O$, which are sensibly the same. The susceptibility measurements on titanium are on the caesium alum, which is of a somewhat different variety, i.e., Lipson and Beevers' "β-type," but the only important change is in the fourth- rather than second-order terms coming from the distant atoms, and the fourth-order portion is significant only for the V rather than Cr or Ti alum (cf. our reference 14). It would be interesting if magnetic data could

nevertheless contribute to the fourth-order trigonal potential, because according to x-ray data the principal axes of the water cluster do not coincide with the principal axes of the crystal. In consequence these ions do not have $\beta_i - \beta_0 = n\pi/3$, and so do not give vanishing results in Eq. (8). Their contribution, however, can readily be computed and is too small to be of any importance.

The two most natural assumptions to make concerning the apportionment of the charge $-2e$ among the members of the SO_4 radical are (a) that S is uncharged and each O carries a mean charge $-\frac{1}{2}e$, or else that (b) S has a charge $+2e$, and each O has $-e$. The truth is doubtless somewhere between (a) and (b), probably closer to (a) than (b);[9] of course, an atom cannot hold instantaneously half an electron, but a mean structure (a) is secured by resonance through various configurations of the form $S(O)_2(O^-)_2$. The second-order part of the field, given by (7), is approximately the same, within ten percent, whether (a) or (b) is used. It gives a splitting of only 40 cm^{-1} in vanadium, of wrong sign, i.e., such that a degenerate state is deepest.[10] The fourth-order terms (8) differ widely with (a) and (b), as the higher harmonics are sensitive to the local arrangement of the SO_4 charge, rather than depending merely on its aggregate amount. With (a), the fourth-order potential is not large enough to overshadow the second-order contribution and to give a substantial splitting of the right sign in vanadium. Instead, the combined separation due to (7) and (8) is practically zero. With model (b), however, the fourth-order effect is considerably greater, so that the resultant splitting amounts to approximately 110 cm^{-1}, and is of such sign that a nondegenerate state is lowest. With either (a) or (b), a nondegenerate level is also deepest in titanium, the splitting Δ shown in Fig. 1 amounting to about 400 cm^{-1} with (a) and 330 cm^{-1} with (b). Both the absolute and relative effects of the various types of terms are quite different in titanium than in vanadium because of the unlike character[10] of the orbital matrix elements for $d^2 D\Gamma_5$ and $d^2\,{}^3F\Gamma_4$.

II. The Indirect Effect of the Field from Distant Atoms

We have seen that with the model $S^{++}(O^-)_4$ of the SO_4 group, the ratio of the second- to the fourth-order terms arising from this radical is such as to make a nondegenerate orbital level the ground state in both V and Ti. The direct effect of the distant atoms may thus, with this particular model, be sufficient to account for the sign behavior of the crystalline potential. Nevertheless, there is no doubt that with any model, this effect is inadequate in magnitude to explain the large over-all width of the Stark splitting. In vanadium, for instance, the latter is of the order 10^3 cm, whereas I gives separations only about one-tenth, or less, of this size. The balance must be attributed to the two remaining factors, II and III, *viz.*, the indirect influence of the field from distant atoms and the Jahn-Teller effect. Study of vanadium alone does not enable one to determine the relative importance of II and III.

However, evidence that II plays an appreciable role is furnished by the empirical magnetic behavior of chrome alum at very low temperatures.[11] The latter[12] demands that the basic spin quartet of chromium split to the extent of about 0.12 cm^{-1}. Now, except for perturbations due to spin-orbit coupling, this quartet should not split at all, since the ground orbital state Γ_2 is nondegenerate. The spin-orbit coupling ultimately spoils the accuracy of the factorization into spin and orbit representations. In consequence, there can be a very small splitting of the quartet, as shown by the detailed calculation to be given in Section IV. This computation may be made with the conventional, one-atom model, and unlike the cases of V and Ti, need not be made with the more complicated Jahn-Teller mechanism, where the seven body system $X\,6H_2O$ must be used as a structural unit. The J-T effect does in principle resolve the quartet, since the spin-orbit inter-

be obtained on the sodium alums, as they are of the γ-type and so unlike the other alums that possibly a different behavior might be found.

[9] The writer is indebted to Professor Linus Pauling for this information.

[10] The splittings produced by the direct field from distant atoms are given by the quantity $3t$ of the following paper, where t is to be computed from its Eqs. (22–24), (34). For the distance R to the molecules of the water cluster, we use the round value 2×10^{-8} cm. The configurations appropriate to the ground states of V and Ti are respectively $d^2\,{}^3F\Gamma_4$, $d^2 D\Gamma_5$, while the excited level of Cr involved in Section IV is $d^3\,{}^4F\Gamma_5$.

[11] Kurti and Simon, private communication.

[12] Hebb and Purcell, J. Chem. Phys. **5**, 338 (1938).

action couples the spin to the crystalline field, and so the J-T displacements can ultimately lift everything but the Kramers degeneracy. The resulting separation of the spin multiplet, however, can be shown[13] to amount to only 10^{-5} cm^{-1}, and so is negligible.

Thus, examination of the magnetic behavior of the ground state of chrome alum has the advantage that the J-T effect drops out, and we need only deal with the other factors I and II. The direct influence of the distant atoms, as we shall see in Section IV, proves capable of giving a splitting of only 0.05 cm^{-1} in the basic quartet. It is immaterial which model of the SO_4 radical is employed, as the fourth-order terms are of subordinate importance in the chromium calculation.[14] The remainder 0.07 cm^{-1} of the total separation 0.12 cm^{-1} must be attributed to the indirect effect of the distant atoms, in virtue of which there is a slight distortion of the nearby water octohedron along the cube body diagonal which coincides with the trigonal axis. The detailed calculation, to be given in Section IV and in the following paper, shows that such a distortion can be quite small, and still adequate to produce a separation of 0.07 cm^{-1} in the chrome quartet. The displacements of the water molecules need only amount to 0.31×10^{-9} cm^{-1} to do this.[15] (The precise value depends on whether the field exerted by the water molecules is regarded as due to point charges or to dipoles; with point charges the estimate is changed to 0.2×10^{-9} cm.) Such small deviations from cubic symmetry are not incompatible with x-ray data, which indicate octohedral grouping, but the experimental precision is only about 3×10^{-9} cm.[16]

If the distortion 0.3×10^{-9} cm^{-1} is present in chromium, it doubtless also occurs in vanadium and titanium, since the corresponding alums are very similar in crystal structure. Now the nice thing that turns out of the calculations of the following paper is that any small distortion of the water cluster compatible with the crystallographic trigonal symmetry gives a sufficiently large ratio of fourth- to second-order terms to make a nondegenerate orbital level appear as the ground state for both titanium and vanadium. The approximate validity of the "spin-only" formula (1) in both alums thus receives a natural explanation in terms of the indirect effect II, without need to worry about the sign behavior of the direct field I, which is probably only of subordinate importance, and which behaves properly only with particular models. The applicability of formula (1) thus cannot be regarded as evidence for model (b), of type $S^{++}(O^-)_4$ for the SO_4 radical, as compared with (a), of type $S(O^{-\frac{1}{2}})_4$. We saw that (b) stabilized the nondegenerate levels in V and Ti, but this fact is irrelevant if II already does the trick. If the distortion amounts to 0.3×10^{-9} cm, then the indirect effect II gives a splitting in vanadium of 425 cm^{-1} (215 cm^{-1} if the charge instead of dipole model is used). It is interesting that an appreciable indirect effect II is demanded by the chrome situation, but even without this evidence, the use of II appears to be the most natural way of explaining the behavior of V and Ti.

At the same time it must be admitted that the sign of the distortion of the water cluster in II has been determined in purely *ad hoc* fashion so as to give the right behavior in Cr, Ti, V. The same sign, to be sure, works consistently in all three cases, and corresponds to the water molecules being repelled away from the trigonal axis. There appears to be no feasible way of finding out whether this sign is that which should occur. One's first guess is perhaps that the distortion is such as to screen rather than, as we have it, reinforce the direct action of the distant field. However, the latter is so feeble, and our concern is with resolution into such high order harmonics, that this simple consideration ceases to be applicable. The outside contacts nearest to a molecule of the water cluster are an exterior water and an oxygen atom.[17] The required sign of the displacement implies that the cluster

[13] See pp. 128–129 of Jahn's paper, reference 7.

[14] The reason that the fourth-order terms are much more perceptible in V than in the other cases is that the ratio of the coefficient of τ_2 to that of τ_1 is much larger in (22b) than in (22c, d) of the following paper.

[15] The displacements required to produce a given splitting $\Delta\nu$ are computed, except for a factor $1/\sqrt{6}$, from the ratios $\Delta\nu/Q_4'$ given in Table II of the following paper. By Eqs. (2) and (5) of the latter, the shift in position of an individual molecule differs from Q_4' by $1/\sqrt{6}$. By our Section IV, the spin separation 0.07 cm^{-1} demands an orbital splitting $\Delta\nu=250$ cm^{-1} in the excited Γ_5 state of Cr.

[16] The writer wishes to thank Drs. Lipson and Beevers for communicating this information to him.

[17] See Fig. 1, p. 678 of Lipson and Beevers, reference 3.

water is repelled by the outside water or attracted by the oxygen. This behavior is not unreasonable, especially as the end of the water dipole nearest the oxygen is positively charged, whereas the oxygen atom is, of course, a negative ion.

III. The Jahn-Teller Effect

Since the Jahn-Teller theorem tells us that stable states are always nondegenerate it may appear that all the magnetic behavior can be explained primarily in terms of the water cluster automatically distorting itself, without invoking I and II. At one time the writer held this view.[18] The two preceding sections, however, have shown that the direct action I of the distant atoms, and especially their indirect effect, II, are not really negligible. Still it may seem that all our worries as to whether I and II are of proper sign to stabilize nondegenerate states are unnecessary, inasmuch as the Jahn-Teller mechanism will come to the rescue and lift any degeneracy otherwise present. If the trigonal field due to I and II is of wrong sign to split the deepest state, the Jahn-Teller effect will secure splitting and removal of the degeneracy only by distorting the water cluster so that the field ceases to be trigonal. This idea of a field of less than trigonal symmetry is not contradicted by magnetic susceptibility measurements. Siegert,[19] to be sure, showed that the behavior of the susceptibility of vanadium alum at low temperatures, where spin-orbit interaction is important, could be explained, in most respects, by assuming a trigonal field. However, it is probable that a field of lower symmetry, say monoclinic or triclinic, would work equally satisfactorily, since then there are two rather than one adjustable parameters, and since the susceptibility in any event approaches a finite limit at $T=0$.

Definite evidence for a field of trigonal symmetry in vanadium is, however, furnished by Gorter's[20] interesting experiments on paramagnetic relaxation, as he has kindly pointed out to the writer. His work shows that at liquid hydrogen temperatures, the absorption in vanadium alum in an oscillating field at frequencies of about 10^7 cycles/sec. is influenced by introduction of a perpendicular magnetic field parallel to the alternating one. This means that the magnetic moment has some exceedingly low frequency, "almost diagonal" matrix elements, involving energy transitions of the order 0.03 cm^{-1} or less. Otherwise the influence of a constant magnetic field would be negligible, since the Zeeman term would merely modify very slightly the intervals between states already widely separated by the crystalline field. Consequently the spin triplet must be incompletely resolved by the crystalline field. (The spin tripling is not to be confused with the much wider separation between three orbital levels shown in Fig. 1. The introduction of the spin triples each of the energy levels in our Fig. 1, and we are concerned only with the decomposition of the lowest level.) Now a field of trigonal symmetry does not resolve the triplet completely, leaving instead a singlet and a doublet so that a positive effect is to be expected in Gorter's relaxation experiment. The doublet will ultimately be very slightly decomposed by dipole-dipole interaction between paramagnetic ions, giving a critical absorption in the region 10^7–10^{11} cycles/sec. or so. Fields of less than trigonal symmetry fully resolve the triplet. The separation between the components is probably of the order 1 to 10 cm^{-1} (by analogy with Siegert's calculation of 5 cm^{-1} for the interval between the singlet and doublet in the trigonal case). A constant magnetic field should then be without effect on the relaxation, contrary to Gorter's experiments. It would be interesting if the latter could be repeated at helium temperatures, as then the upper or doublet level in the trigonal case becomes virtually uninhabited, and a constant magnetic field should be without much effect even with trigonal symmetry.

It is to be pointed out that when the Jahn-Teller effect "rescues" the atom from a degenerate trigonal state, it is only the instantaneous field which is of less than trigonal symmetry. As the detailed calculation of the next paper, or general considerations of symmetry show, there are always three possible directions of distortion from trigonal symmetry which are on a par. Because of the "tunnel" effect, there is bound to be resonance through the different equivalent configurations. The situation is somewhat similar to that in the familiar example[21] of the NH_3 mole-

[18] J. H. Van Vleck, Phys. Rev. **52**, 246(A) (1937).
[19] Siegert, Physica **4**, 138 (1937); van den Handel and Siegert, *ibid.* **5**, 871 (1938).
[20] C. G. Gorter, Physica, **3**, 1006 (1936).
[21] Cf. Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932); Rosen and Morse, *ibid.* **42**, 210 (1932).

cule, which is continually resonating or turning itself inside out. The time exposure charge cloud, obtained by averaging over the resonance, thus has the full trigonal symmetry. There is then no contradiction between the concept of instantaneous fields of less than trigonal symmetry, and the crystallographic classification indicated by the x-ray evidence, which is known to be $Pa3T_h^6$, and which demands that the environment of a given paramagnetic ion have trigonal symmetry. The latter, however, need relate only to the time average. The question arises whether the resonance through the various configurations could be detected by x-ray measurements. As the H_2O molecules would have several possible locations, there should be a diffuseness or fuzziness in their positions. However, it is very doubtful whether the diffuseness would be sufficient to be detectable, as the difference in position between the various configurations participating in the resonance probably amounts to only 10^{-9} cm or so. If the splitting due to the tunnel effect or resonance between the various equivalent configurations is very large compared to the spin splitting, the resonance is too rapid for the spin to follow. Then the time exposure field is more important than the instantaneous field, and the difficulty connected with paramagnetic relaxation might be avoided. However, estimates of the size of the hill to be tunneled through indicate that the tunnel splitting is probably of about the same size as for NH_3. (In NH_3, resonance doubling[21] amounts to 0.4 cm^{-1} and 40 cm^{-1}, respectively, for states with zero and one quantum of vibration; the barrier for the latter is probably a little nearer ours than is the former.) We should thus expect a series of levels separated by 1 to 10 cm^{-1} or so, a distance not large compared to the spin splitting, which is of the same order (cf. Siegert's[19] estimate of 5 cm^{-1} in vanadium). The spin is thus able to respond, at least partially, to the instantaneous field.

It would be interesting if a physical case could be found where the cluster $X \cdot 6H_2O$ resonates through a variety of Jahn-Teller configurations, as then we would have a nice example of a characteristic quantum-mechanical effect. We have seen that this situation is unlikely in vanadium. The susceptibility measurements, rather meagre, anyway, do not seem to preclude it in titanium alum. Here there is no conflict with paramagnetic relaxation, as there is always the Kramers twofold degeneracy and so the J-T effect cannot split the doublet. The tunnel splitting would not affect the susceptibility in a major way, but should give pronounced anomalies in the specific heat. Our calculations indicate that it is probable that a nondegenerate trigonal state is deepest in titanium alum. If so, the resonance situation should not occur here. There is, however, no reason it should not frequently arise in excited states, for example the upper levels in Spedding and Nutting's Zeeman observations[22] in chrome alum which we will discuss in a later paper, or perhaps sometimes in the ground states of other salts than the usual alums.

In summary, we can say that it appears necessary that a nondegenerate trigonal state be deepest in vanadium alum, and that the Jahn-Teller effect is not the primary agency in bringing this about. However, this does not mean that this effect is unimportant, as it plays an important role in amplifying the splitting and making it about twice as large as it would be otherwise. In a certain sense, the J-T mechanism is intimately connected with the existence of an appreciable indirect effect II of the distant atoms. The essence of the J-T theorem is that a degenerate ion feels any displacements in the surrounding atoms in the first order rather than the second as in the usual equilibrium theory, and it is for this reason that the polarization of the water cluster involved in II can be so important.

To determine the total displacement of the water molecules from the octohedral configuration, we must add the distortion due to the J-T mechanism (given[15] by $Q_4'/\sqrt{6}$, with Q_4' as in Table II of the following paper) to that due to the indirect effect of the distant atoms estimated in the preceding Section II. The total displacement, thus augmented, then aggregates 0.63×10^{-9} and 0.67×10^{-9} cm in V and Ti, respectively, (0.44×10^{-9} and 0.75×10^{-9} if the charge rather than dipole model is used). These shifts are still apparently too small to detect by x-ray technique, as they are about one-fourth of the latter's precision.

It is tempting to try and calculate the total splitting in vanadium and titanium by computing I and III directly with particular models, and determining the extent of II from the part of the chromium splitting not attributable to I. Then effects I, II, III (direct, indirect, distant, J-T, respectively) contribute 0 (or 110[23]), 425, 435 cm^{-1} to the total splitting in vanadium shown in Fig. 1, which then aggregates 860 cm^{-1}. The corresponding figures for titanium are 400, 500, 550, totaling 1450 cm^{-1}. These estimates are of a reasonable order of magnitude, and that is about all that can be said, for too much quantitative significance should not be attached to the theoretical computations, and there is also uncertainty in the empirical splittings deduced from the experimental data. As an indication of the leeway in the calculated values, we may

[22] Spedding and Nutting, J. Chem. Phys. **3**, 369 (1935).

[23] The values 0 and 110 cm^{-1} relate respectively to models (a) and (b) of Section II.

mention that if the charge rather than dipole model of the water cluster is employed, the values for V become 0, 215, 245, totaling 460 cm^{-1} and for Ti, 400, 500, 1320, totaling 2220 cm^{-1}.

Unfortunately the susceptibility of titanium alum has not been measured over a wide temperature range, so that there is no experimental evidence on the splitting.[24] The value for vanadium is of the order 10^3 cm^{-1}, but there is considerable ambiguity on the precise magnitude, as we discuss in detail below in fine print.

Siegert's theory and the Stark splitting of vanadium alum.— From susceptibility data, van den Handel and Siegert[19] calculate 700 cm^{-1} for the trigonal splitting in vanadium alum, but this is under the assumption that the cubic field is so powerful as to break down the Russell-Saunders (*ll*) coupling. If instead this coupling is a good approximation, this estimate should be increased by a factor $(\frac{3}{2})^2$. As we will show elsewhere, the Russell-Saunders assumption is closer to the truth than the breakdown one. We estimate the proper correction factor to be in the neighborhood of 1.34, so that Siegert's estimate[25] of 700 cm^{-1} is changed to 1300 cm^{-1}.

In any case, deductions of the splitting from Siegert's susceptibility theory are rather uncertain inasmuch as the latter does not fit all the facts. There are essentially three major items which the theory must yield: (a) a splitting of the spin triplet by about 5 cm^{-1}, in connection with the departure of the susceptibility from Curie's law at low temperatures, (b) a reduction of the Curie constant of about 8 percent from the spin-only value given by Eq. (1), and (c) a constant term 0.3×10^{-6} independent of temperature in the expression for the susceptibility per unit mass. Van den Handel and Siegert choose to fit (a) and (b), but obtain a value of (c) three times too high. In so doing, they are forced to use a spin-orbit parameter about 40 percent lower than the spectroscopic value. Possibly this is allowable because forces in the solid state spoil the diagonality in the principal quantum number, but on the other hand Krishnan[26] is successful in explaining anisotropy in other iron salts with the normal spectroscopic value. If one fits (a) and (c), and sacrifices (b),[25] an approximately normal value of the spin-orbit parameter results, but the splitting is increased to 3×1300 or about 4000 cm^{-1}, a value doubtless too high.

Very likely, the difficulty in explaining (a), (b), (c) is because the susceptibility cannot really be treated as a one atom problem, since the Jahn-Teller effect, or in other words linearity of the potential in the water molecules' coordinates, makes the latter's vibrations have some repercussion on the susceptibility. One of the main points we wish to convey in the present paper is that the whole cluster $V6H_2O$ rather than merely V ought really to be considered as the structural unit. However, the proper calculation would be very difficult, and it is not clear whether the modifications would be important, or in the right direction. One can show that in a first approximation the vibrational effects do not modify the results if a suitable centroid frequency or separation be used. This separation can be shown to be the same as that which would result if the H_2O molecules occupied the same positions in the upper states as in the equilibrium configuration for the ground level. Actually, the J-T effect makes the equilibrium positions different for the excited than for the ground state. There are bound to be some small corrections to any calculation made with a centroid or one-atom model. In particular, as the temperature is raised and quanta of vibration are excited, the atom wanders a little from its equilibrium position even in the ground state. At these other positions the upper levels may be somewhat lower than before, whereas the ground level is, of course, higher. In consequence the effective Stark splitting, and hence, the apparent Curie constant may decrease with increasing temperature. This effect may mask the true, relatively insignificant constant term, so that the apparent experimental value of the latter is too small.

IV. Chrome Alum

In chromium, unlike titanium or vanadium alum, the deepest orbital state of the ion in a purely cubic field is nondegenerate, *viz.*, Γ_2 in Bethe's notation. The configuration d^3, here involved, also gives two threefold orbital levels in a cubic field, *viz.*, Γ_5 and Γ_4, but these states are two or three volts higher. Hence the J-T mechanism is not required to lift the orbital degeneracy of the normal term. It is a great merit of the J-T effect that it disappears when not needed. Namely, in a nondegenerate state the energy involves the displacements of the surrounding water molecules only through squares rather than through the first powers which are characteristic of the J-T theory. In other words, the cubic configuration is now perfectly stable, except as distorted by forces from distant atoms. Since the orbital angular momentum is quenched by a cubic field, rather than by the smaller, less symmetrical portions of the field as in Ti^{+++} and V^{+++}, the g factor in Cr^{+++} is exceedingly

[24] In Ti, the splitting Δ shown in Fig. 1 should manifest itself through a constant term of magnitude $4N\beta^2/3\Delta$, independent of temperature, in the susceptibility.

[25] Our statements concerning how the parameters depend on the various conditions are consequences of the fact that the low temperature spin splitting, the reduction in the Curie constant, and the temperature-independent term are respectively proportional, approximately to K^2A^2/Δ, K^2A/Δ, K^2/Δ where A is the spin-orbit parameter, Δ is the trigonal splitting, and K ranges from 1 to $\frac{3}{2}$ depending on the type of coupling.

[26] Krishnan and Bose, Nature **141**, 329 (1938).

close to 2 and the spin-only formula applies much more closely than usual. $CrCl_3$, the only chromic salt whose gyromagnetic ratio has been measured,[27] has $g=1.95$.

Though a cubic field lifts the orbital degeneracy in Cr^{+++}, group theory shows that it will not split the spin multiplet, here a quartet. This is reflected in the fact that experimentally the susceptibility of chromic alum, including the saturation behavior in strong fields, conforms very perfectly to the spin-only formula even at the lowest helium temperatures. However, measurements of the specific heat of chrome alum in the new domain of very low temperatures obtained by magnetic cooling, indicate that the ground quartet does split[12] to the extent of about 0.12 cm^{-1}. The quartet, of course, cannot separate into more than two components, for the Kramers twofold degeneracy must be preserved since there are an odd number of electrons. This small splitting is to be contrasted with that[19] of 5 cm^{-1} in V^{+++}, where the quenching of the spin-orbit coupling takes place only in virtue of the noncubic portion of the crystalline field, and so is much less complete.

The splitting of the quartet revealed by the specific heat measurements implies that the field acting on the spin is not accurately cubic, probably instead trigonal. Then the energy is slightly different for the pair of states $M_S=\pm\frac{1}{2}$ than for $M_S=\pm\frac{3}{2}$, where M_S is the component of spin parallel to the trigonal axis. This resolution of the ground quartet is a reflection of the fact that the trigonal field splits the excited triply degenerate cubic state Γ_5 into a twofold level E and a single one A. (The upper state Γ_4 is also split, but this is not connected with the ground state by matrix elements of spin-orbit interaction, and so does not concern us.) The spin-orbit energy may be regarded as a perturbation which couples together the ground with the excited state, and so makes the spin multiplet of the ground level indirectly experience the trigonal splitting in the upper state. Without the influence of the upper state, the quartet would be unresolved, since the deepest orbital level is nondegenerate.

We now present the details of the perturbation calculation giving the amount of splitting of the quartet. As explained in Section II this computation may be made with the conventional one-atom model, and, unlike the cases of V and Ti, need not be made with the more complicated, Jahn-Teller mechanism, where the seven body system $Cr6H_2O$ must be used as a structural unit.

The matrix elements of the components of angular momentum L_x, L_y, L_z joining the ground state Γ_2 to the various components of Γ_4 and Γ_5 all vanish except that

$$L_z(\Gamma_2 A\,;\,\Gamma_5 A)=L_x(\Gamma_2 A\,;\,\Gamma_5 E^+)$$
$$=L_y(\Gamma_2 A\,;\,\Gamma_5 E^-)=2. \quad (10)$$

Here the first index Γ gives the cubic representation, and the second (A, E) the trigonal representation of the various components into which the cubic levels are resolved by a trigonal field. The Γ notation is that of Bethe, and the A, E that of Mulliken. The substates of E have been denoted by E^+, E^-.

The result (10) can be obtained by writing down explicitly the wave functions appropriate to the various Stark components, and then computing the matrix elements in the usual way. These functions are published elsewhere by Opechowski,[28] in connection with a different problem. It is, however, not necessary to employ the detailed wave functions, as group theory shows that $\mathbf{L}$ joins Γ_2 only to Γ_5 and not to Γ_4; furthermore L_z can only connect A with A while L_x, L_y join A only to E. If the azimuthal factors of E are real, then L_x and L_y cannot end on the same component of E. (The group basis of these statements is that $\mathbf{L}$, L_z, (L_x, L_y) transform like Γ_4, A, E, respectively, and that $\Gamma_2\times\Gamma_4=\Gamma_5$, $A\times A=A$, $A\times E=E$.) The equality of the various elements in (10), except for phase, is required by the fact that the Γ's are cubic representations, and the value 2 results from the fact that the squares of the components must sum to $L(L+1)=12$.

[27] W. Sucksmith, Proc. Roy. Soc. **133**, 179 (1932). $CoSO_4$ has a g factor only 1.54. This fact may seem to belie our statement that the Jahn-Teller mechanism always lifts the orbital degeneracy. However, in elements such as cobalt, well to the right in the iron period, it is not allowable to treat the spin-orbit coupling as small in comparison with the J-T effect, as we do in the following paper.

[28] W. Opechowski, note on the paramagnetic rotation of nickel salts at low temperatures, to appear, probably, in some French journal.

We now use the second-order perturbation formula

$$\delta W = \Sigma_i H(ij)^2/h\nu(ij) \qquad (11)$$

taking $H = A\mathbf{L}\cdot\mathbf{S}$. Each state i or j is specified by two indices: one the orbital designation such as $\Gamma_2 A$, etc., the other the value of the spin quantum number M_S, the component of S parallel to the trigonal axis and which takes on the values $M_S = \pm\frac{1}{2}, \pm\frac{3}{2}$. The matrix elements of $\mathbf{S}$ are

$$S_x(\pm\tfrac{1}{2};\pm\tfrac{3}{2}) = \pm iS_y(\pm\tfrac{1}{2};\pm\tfrac{3}{2}) = \sqrt{\tfrac{3}{4}},$$
$$S_x(\pm\tfrac{1}{2};\mp\tfrac{1}{2}) = \mp iS_y(\pm\tfrac{1}{2};\mp\tfrac{1}{2}) = 1,$$
$$S_z(\pm\tfrac{3}{2};\pm\tfrac{3}{2}) = \pm\tfrac{3}{2}, \qquad S_z(\pm\tfrac{1}{2};\pm\tfrac{1}{2}) = \pm\tfrac{1}{2}.$$

If ν_c and $\nu_c+\Delta$ be, respectively, the distances of $\Gamma_5 A$ and $\Gamma_5 E$ above the ground state, then one finds

$$\delta W(\tfrac{3}{2}) = \delta W(-\tfrac{3}{2}) = -A^2((9/h\nu_c)+6/(h\nu_c+\Delta)), \qquad (12)$$

$$\delta W(\tfrac{1}{2}) = \delta W(-\tfrac{1}{2}) = -A^2((1/h\nu_c)+14/(h\nu_c+\Delta)). \qquad (13)$$

Since $\delta/h\nu_c$ is small

$$\delta W(\tfrac{1}{2}) - \delta W(\tfrac{3}{2}) = 8\Delta A^2/h^2\nu_c^2. \qquad (14)$$

Spectroscopic data show that A is about 87 cm^{-1}. Unlike the case of vanadium, this estimate is not changed by the incipient breakdown of Russell-Saunders coupling. The reason for this statement is that the configuration d^3 contains the representations Γ_2 and Γ_5 each only once with $S=\frac{3}{2}$, and so a cubic potential will not blend the states with which we are concerned with other states, while any trigonal mixing is negligible. We may take $h\nu_c = 15{,}000$ cm^{-1}, as $h\nu_c$ is 10 times the constant Dq which we estimate in the following paper to be about 1500 cm^{-1}. Then if the expression (14) is to have the magnitude +0.12 cm^{-1} observed experimentally, we must have $\Delta = 450$ cm^{-1}. This value is reasonable in size. The direct effect I of the distant atoms would give[29] a splitting of 200 cm^{-1}, which would correspond to a separation of 0.05 cm^{-1} in the basic quartet, and the balance is to be attributed to the indirect effect, as explained in Section II. Too much quantitative accuracy should not be attached to the splitting 0.12 cm^{-1} deduced from the low temperature data, but a value as low as 0.05 cm^{-1}, which would eliminate the indirect effect, appears out of the question. It is particularly interesting to note that the sign is what our theory would predict; namely, the contributions of both the direct and indirect effects of the distant atoms to Δ are positive, so that $\Delta > 0$. The first contribution is positive according to our attempts in Section I to compute the potential from the charges' positions, while the second is positive if the sign of the polarization of the water cluster is such as to make a non-degenerate state deepest in vanadium. We thus have an independent confirmation, quite apart from low temperature analysis, of Hebb and Purcell's conclusion that $M_S = \pm\frac{3}{2}$ is deeper than $M_S = \pm\frac{1}{2}$.

[29] This splitting is computed as explained in reference 10. If model (b) rather than (a) of Section II is used, the estimate is changed to about 150 cm^{-1}; the resulting alteration in the balance to be attributed to the indirect effect II is too small to be important for our crude estimates. In the following paper we compute appreciable Jahn-Teller splittings for the Γ_5 state of Cr. However, these splittings are irrelevant for our purposes, because our quantity Δ relates to the separation exclusive of the J-T effect, inasmuch as the perturbation calculation involves the time average configuration for the excited state. (This averaging does not appear explicitly, but arises because a detailed calculation allowing for vibrational structure would involve summation over the various vibrational substates and J-T configurations.) Because of resonance, the average symmetry is not affected by the J-T effect, as explained in fine print in Section III.

The Jahn-Teller Effect and Crystalline Stark Splitting for Clusters of the Form XY_6

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The present article develops the mathematical theory needed in connection with the preceding paper, and with a study of paramagnetic relaxation to appear later. Jahn and Teller have shown that the normal coordinate theory for a molecular cluster such as $X \cdot 6H_2O$ (X = Ti, V, Cr) is materially different from usual if the X ion is degenerate. Namely, it is impossible to eliminate linear terms in the atomic displacements simultaneously from all substates of the degenerate level. Consequently, stability is achieved only if the degeneracy is lifted, and so the water group distorts itself so that it is not cubically arranged. A calculation is made of the magnitude of the effect, which has an important bearing on magnetic behavior. In order to allow for the disturbing effect of distant atoms, the cluster $X \cdot 6H_2O$ is not treated as free, but rather as embedded in a trigonal field of force. The Stark splittings in such fields, quite apart from the Jahn-Teller effect, are hence obtained as a corollary.

1. Introduction

JAHN and Teller[1] have shown that if there is a degenerate electronic state, stability considerations and the theory of normal coordinates are profoundly modified. Linear terms will appear in the expansion of the potential energy in terms of the vibrational displacements, which can be eliminated only if the system is so distorted as to give enough asymmetry to lift the degeneracy (except, of course, for the inherent Kramers twofold degeneracy in odd systems). The physical reason for this phenomenon is, essentially, that in a degenerate system, the electronic charge cloud has different orientations for different components of the degenerate family. Hence the linear terms in the normal coordinates cannot be simultaneously eliminated for all components, and the persistence of the linear terms means distortion and lowered symmetry.

In the present paper we will treat a group of the form XY_6, as this is of particular interest for the theory of magnetism, where X signifies a paramagnetic ion, and Y a water molecule. The physical conclusions based on the mathematics of the present analysis are discussed in the preceding article.[2] Applications to paramagnetic relaxation which are made by expanding the normal coordinate in terms of Debye waves will be treated in a later paper. They materially reduce, especially for titanium, the excessive relaxation times previously computed by other authors. Besides the interest in connection with magnetism, we believe the present paper has perhaps some use as a concrete illustration of the Jahn-Teller effect, the theory of which was originally presented in rather abstract form.

2. The Normal Coordinates

The subscripts 0 and $1 \cdots 6$ will relate respectively to the center (X) and corner (Y) atoms. Let x_0, y_0, z_0 be the Cartesian coordinates of a d electron of the central atom, and let x_i, y_i, z_i be the Cartesian coordinates of atom $i (i = 1, \cdots 6)$. It is not necessary for us to probe into the electronic structure of the corner atoms. On the other hand, the d shell will in general contain more than one electron, and so there will be several different x_0, y_0, z_0 over which we must sum the potential energy. Let x_i^0, y_i^0, z_i^0 be the values of x_i, y_i, z_i appropriate to perfect octohedral arrangement. Here we may suppose atoms 1, 2, 3 located respectively on the x, y, z coordinate axes, and atoms $i, i+3$ on opposite sides of the central atom. Thus

$$x_0^0, y_0^0, z_0^0 = 0, 0, 0; \quad x_1^0, y_1^0, z_1^0 = R, 0, 0; \quad x_2^0, y_2^0, z_2^0 = 0, R, 0; \quad \cdots x_4^0, y_4^0, z_4^0 = -R, 0, 0, \text{ etc.} \qquad (1)$$

[1] H. A. Jahn and E. Teller, Proc. Roy. Soc. **161**, 220 (1937); H. A. Jahn, *ibid.* **164**, 117 (1937).
[2] J. H. Van Vleck, J. Chem. Phys. **7**, 61 (1939).

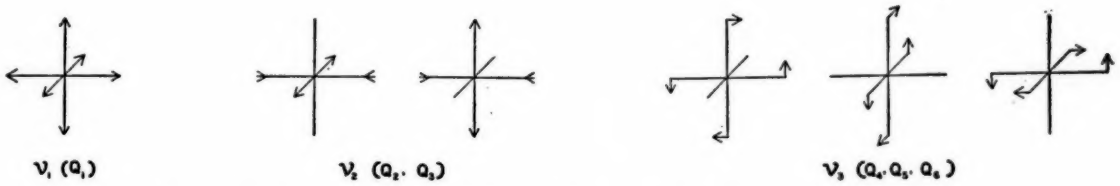

FIG. 1. The symmetrical (g) nodes of vibration of an octohedral complex XY_6.

where $2R$ is the width of the cube whose face centers are occupied by the six Y atoms. Let X_i, Y_i, Z_i be the displacements of an atom from the ideal octohedral arrangement (1), so that $X_i = x_i - x_i^0$, etc.

In place of the X, Y, Z we now introduce new variables which would be normal coordinates[3] for a nondegenerate XY_6 group. The corresponding modes of vibration are shown in Fig. 1. The first six of these coordinates are of even or symmetric type, and can be taken to be

$$\left.\begin{aligned} Q_1 &= [X_1 - X_4 + Y_2 - Y_5 + Z_3 - Z_6]/\sqrt{6}, & Q_4 &= \tfrac{1}{2}[Y_1 - Y_4 + X_2 - X_5], \\ Q_2 &= \tfrac{1}{2}[X_1 - X_4 - Y_2 + Y_5], & Q_5 &= \tfrac{1}{2}[Z_1 - Z_4 + X_3 - X_6], \\ Q_3 &= [\tfrac{1}{2}(X_1 - X_4 + Y_2 - Y_5) - Z_3 + Z_6]/\sqrt{3}, & Q_6 &= \tfrac{1}{2}[Z_2 - Z_5 + Y_3 - Y_6]. \end{aligned}\right\} \quad (2)$$

The definition of the remaining nine normal coordinates $Q_7, \cdots Q_{15}$ need not concern us. They are of the odd or u type under the reflection in the origin $x = -x$, $y = -y$, $z = -z$, $i = i \pm 3$ and so introduce no linear terms in the Hamiltonian function. This fact can be seen either by explicit expansion of a potential such as (9) to be given later, or more elegantly by using Jahn and Teller's result that only those displacements give rise to linear terms whose representations are contained in the symmetrical direct product of the representation of the central atom's ground level with itself. The symmetrical direct product is easily seen to contain no u representations. On the other hand, group theory shows that $Q_2, \cdots, Q_6$ can give rise to linear terms in the Hamiltonian function, as we verify in detail later. Without loss of generality, we may suppose that there are no linear terms in Q_1. Otherwise we would scarcely have a starting point. Thus, we may assume that (1) represents equilibrium as far as a totally symmetric vibration is concerned. The gist of the Jahn-Teller theorem is the fact that with orbital degeneracy, it is impossible to eliminate linear terms for all types of displacement and for all Stark components. However, it is still possible to eliminate such terms on the average, and this is essentially what is done in supposing that our point of departure represents equilibrium as far as the normal coordinate Q_1 is concerned.

A cluster such as XY_6 obviously has 21 degrees of freedom, but we have cited only 15 normal coordinates. The remaining variables $Q_{16}, \cdots, Q_{21}$ are merely translations or rotations. Translations have u symmetry, and are of no interest to us. The coordinates Q_{19}, Q_{20}, Q_{21} which are simple rotations are

$$Q_{19} = \tfrac{1}{2}[X_2 - X_5 - Y_1 + Y_4], \quad Q_{20} = \tfrac{1}{2}[Z_1 - Z_4 - X_3 + X_6], \quad Q_{21} = \tfrac{1}{2}[Y_3 - Y_6 - Z_2 + Z_5]. \quad (3)$$

In place of (3), it is often convenient to use the following orthogonal linear combinations

$$Q_{19}' = [Q_{19} + Q_{20} + Q_{21}]/\sqrt{3}, \quad Q_{20}' = [Q_{20} - Q_{21}]/\sqrt{2}, \quad Q_{21}' = [Q_{20} + Q_{21} - 2Q_{19}]/\sqrt{6}. \quad (4)$$

Corresponding combinations of Q_4, Q_5, Q_6 will also often be used:

$$Q_4' = [Q_4 + Q_5 + Q_6]/\sqrt{3}, \quad Q_5' = [Q_5 - Q_6]/\sqrt{2}, \quad Q_6' = [Q_5 + Q_6 - 2Q_4]/\sqrt{6}. \quad (5)$$

The expressions (5) serve as normal coordinates equally well in place of Q_4, Q_5, Q_6.

[3] Yost, Steffens, and Gross, J. Chem. Phys. 2, 311 (1934). Our coordinate Q_3 is a linear combination of the two modes ν_2 in Fig. 1, rather than one of the modes taken separately.

3. The Hamiltonian Function

The Hamiltonian function may be taken to be

$$H=W_0+V_{\text{trig}}+V_2Q_2+V_3Q_3+V_4'Q_4'+V_5'Q_5'+V_6'Q_6'+V_{19}'Q_{19}'+V_{20}'Q_{20}'+V_{21}'Q_{21}' \tag{6}$$

with

$$\begin{aligned}W_0=V_{\text{cubic}}&+cQ_4'+\tfrac{1}{2}\alpha Q_1^2+\tfrac{1}{2}\beta(Q_2^2+Q_3^2)+\tfrac{1}{2}\gamma Q_4'^2+\tfrac{1}{2}\delta(Q_5'^2+Q_6'^2)+\tfrac{1}{2}\zeta Q_{19}'^2+\tfrac{1}{2}\eta(Q_{20}'^2+Q_{21}'^2)\\&+\theta Q_1Q_4'+\kappa(Q_2Q_5'+Q_3Q_6')+\chi Q_1Q_{19}'+\omega Q_4'Q_{19}'+\lambda(Q_2'Q_{20}'+Q_3'Q_{21}')\\&+\nu(Q_5'Q_{20}'+Q_6'Q_{21}')+\Sigma_{i,\ j=7,\ \cdots 18}\xi_{ij}Q_iQ_j.\end{aligned} \tag{7}$$

The coordinates $Q_7, \cdots, Q_{18}$ are all odd (u) as regards reflection in the origin, and their part of the secular problem factors off completely from that in which we are interested.

In writing (6, 7), we have assumed that the cluster XY_6 is not entirely free, but instead is subject to an external field from the other atoms in the crystal. In accordance with x-ray data on the alums,[4] we assume that this field has trigonal symmetry. For applications to molecular spectra, we are interested merely in the free molecules XY_6 as such, but in connection with magnetism, it is imperative to include an external field, since here the cluster XY_6 is embedded in the crystal.

It is important that the reader have a clear appreciation of the nature of the expressions V_{cubic}, V_{trig}, $V_2, \cdots, V_6'$. They are to be understood as follows:

V_{cubic} is a function of the coordinates of the d electrons of the central atom, and involves as parameters the undistorted positions of the other atoms. By hypothesis, V_{cubic} has cubic symmetry and is by far the largest term in the potential. It arises partly from the forces exerted on the central ion by atoms exterior to the cluster, but mainly from the coupling of this ion to the six Y atoms (really six water molecules), which have octohedral symmetry at their unperturbed positions. In addition, V_{cubic} can embody the mutual energy connecting different Y atoms with each other, but this part of the energy is of no importance for us, as it does not involve the coordinates of the central atoms.

We shall assume that in our secular problem, the "unperturbed" orbital wave functions of the central atom are such as to diagonalize V_{cubic}. These functions then transform according to irreducible representations of the cubic group. Throughout, we neglect the disturbing effect of spin-orbit interaction, as the empirical magnetic data, discussed in the preceding paper, show it is of subordinate importance in the first approximation.

V_{trig} is the potential which the central atom experiences because the atoms in the crystal, other than the surrounding Y group, are arranged with only trigonal symmetry in the alums and yields what we called the "direct field due to distant atoms" in the preceding article. In other words, it is the correction because the potential due to the next to nearest and more remote neighbors of the central atom is not strictly cubic. It does not arise at all from forces from the Y molecules, as, at their unperturbed positions (1), they are arranged with perfect cubic symmetry. In this respect, V_{trig} differs from V_{cubic} which is due mainly to forces from the nearest neighbors Y. Even the latter are, quite apart from the J-T effect, probably not accurately arranged in an octohedron, because of disturbances caused by the trigonal field exerted by distant atoms. To allow for this possibility, we have added the term cQ_4' in (7), which, though linear in Q, is not a manifestation of the Jahn-Teller effect. Instead it is an expression of the fact that even without this effect, or in other words, even if the central atom is nondegenerate, the equilibrium arrangement of the six corner atoms in the crystal does not necessarily have octohedral symmetry, but corresponds rather to a distortion of the cube along a body diagonal which is the axis of trigonal symmetry. Such a distortion corresponds to a displacement in Q_4' with the other Q's held fixed, and the absence of equilibrium, of course,

[4] H. Lipson and C. A. Beevers, Proc. Roy. Soc. **148**, 664 (1935); H. Lipson, *ibid.* **151**, 347 (1935).

means the possible existence of a linear term. The coefficient c of this extra term cannot be evaluated unless the forces from the distant atoms are known in detail, which is not the case. We have supposed that the axis of trigonal symmetry is $x=y=z$. This involves no loss of generality. As a matter of fact only one-fourth of the XY_6 clusters have this direction for the trigonal axes, as there are four trigonal axes appearing in the unit cell, each involving one X atom. Nevertheless our choice represents a typical situation. The repercussions of the cQ_4' term on the Stark splitting of the central ion embody what we called the indirect effect of the distant atoms in the preceding paper.

There is some evidence from x-rays that the axes of the water octohedron do not quite coincide with the principal cubic axes of the crystal, which we take as our x, y, z system. In other words, the octohedron is given a slight twist about the trigonal axis, without deformation. Such a twist is embodied in our rotational coordinates Q_{19}', Q_{20}', Q_{21}' and is easily seen to give rise to only a quadratic term in the Hamiltonian function. The perturbation caused by the noncoincidence of the two sets of cubic axes is consequently negligible.

The terms $V_2\cdots V_6'$ are the essence of the Jahn-Teller effect, as they are linear rather than quadratic in the normal coordinates. With our choice (2) of normal coordinations, the transformation schemes of $Q_1, \cdots, Q_6'$, of their coefficients $V_2, \cdots, V_6'$, and of the rotations $Q_{19}', \cdots, Q_{21}'$ are as follows, in Bethe's notation[5]

$$\begin{array}{cccc} \Gamma_{1g} & \Gamma_{3g} & \Gamma_{4g} & \Gamma_{5g} \\ Q_1 & Q_2, Q_3 & Q_{19}, Q_{20}', Q_{21}' & Q_4', Q_5', Q_6' \\ & V_2, V_3 & & V_4', V_5', V_6'. \end{array}$$

This classification also applies if the primes are omitted. The coefficients V_2, V_3 will be nonvanishing if the degenerate orbital state is any one of the three possible types Γ_3, Γ_4, Γ_5. On the other hand V_{19}', V_{20}', V_{21}' will vanish for all three cases and V_4', V_5', V_6' will differ from zero only for Γ_4 and Γ_5. These facts can be seen not only from the calculations with an explicit model, to be given later, but also more elegantly from the Jahn-Teller theorem that the coefficients will be nonvanishing if the vibration corresponding to Q is of a type contained in the symmetrical product of the representation of the orbital state with itself. The appropriate reductions of the symmetrical product are[1]

$$[\Gamma_3\times\Gamma_3]_{\text{sym}}=\Gamma_{3g}, \quad [\Gamma_4\times\Gamma_4]_{\text{sym}}=[\Gamma_5\times\Gamma_5]_{\text{sym}}=\Gamma_{1g}+\Gamma_{3g}+\Gamma_{5g}. \tag{8}$$

There is no coefficient V_1 of Q_1, because our coordinates have the normal property for totally symmetric vibration, as already explained.

The coefficients $V_2\cdots V_6'$ are functions of the coordinates x_0, y_0, z_0 of the d electrons, and depend on the nature of the force connecting the central atom X with the corner atoms Y. They are not affected by the forces between the corner atoms, as the latter contribute only to the constant term V_{cubic} and to the quadratic terms in the Q's. If these corner atoms can be regarded as isotropic, though not necessarily Coulomb force centers, the mutual energy depends only on distance, and the potential of the d electrons due to the corner atoms is

$$V=\sum_0\sum_{i=1,\ \cdots,\ 6} f(r_{0i}). \tag{9}$$

Here the sum over 0 means summation over all the d electrons of the center atom, and

$$r_{0i}^2=(x_i^0+X_i-x_0)^2+(y_i^0+Y_i-y_0)^2+(z_i^0+Z_i-z_0)^2.$$

Clearly

$$V_j=\sum_{i=1,\ \cdots,\ 6}\left(\frac{\partial V}{\partial x_i}\frac{\partial x_i}{\partial Q_j}+\frac{\partial V}{\partial y_i}\frac{\partial y_i}{\partial Q_j}+\frac{\partial V}{\partial z_i}\frac{\partial z_i}{\partial Q_j}\right). \tag{10}$$

[5] For the group theory methods used in connection with the crystalline Stark effect, see H. Bethe, Ann. d. Physik **3**, 133 (1929); R. S. Mulliken, Phys. Rev. **43**, 279 (1933).

Now because of the unitary character of the transformations from the x, y, z to the normal coordinates, we have $\partial x_i/\partial Q_j=\partial Q_j/\partial x_i$ and we find from (9), (10) and (2)

$$V_2=\tfrac{1}{2}[r_{01}^{-1}f_{01}'(R-x_0)-r_{04}^{-1}f_{04}'(-R-x_0)-r_{02}^{-1}f_{02}'(R-y_0)+r_{05}^{-1}f_{05}'(-R-y_0)], \tag{11}$$

where f_{0i}' means $\partial f_{0i}/\partial r$ evaluated at the unperturbed position of the corner atom, but not with the d electrons in general at the origin. Similarly

$$V_3=(1/\sqrt{3})\textstyle\sum_0[\frac{1}{2}r_{01}^{-1}f_{01}'(R-x_0)-\frac{1}{2}r_{04}^{-1}f_{04}^{-1}(-R-x_0)+\frac{1}{2}r_{02}^{-1}f_{02}'(R-y_0)$$
$$-\tfrac{1}{2}r_{05}^{-1}f_{05}'(-R-y_0)-r_{03}^{-1}f_{03}'(R-z_0)+r_{06}^{-1}f_{06}'(-R-z_0)],$$
$$V_4=\tfrac{1}{2}\textstyle\sum_0[-r_{01}^{-1}f_{01}'y_0+r_{04}^{-1}f_{04}'y_0-r_{02}^{-1}f_{02}'x_0+r_{05}^{-1}f_{05}'x_0], \quad \text{etc.}$$

Here V_4, V_5, V_6 are similar to V_4', V_5', V_6' except that they are coefficients appropriate to the expansion (6) in terms of unprimed variables. If we assume that the radius r_0 of the d shell is small compared with the interatomic separation R, the quantities $r_{0i}^{-1}f_{0i}'$ may be developed as an ascending series in r/R. Then $V_2, \cdots, V_6$ have the form

$$\begin{aligned} V_2&=\textstyle\sum_0\{A(x_0^2-y_0^2)+B(x_0^4-y_0^4)\}+\cdots, \\ V_3&=\textstyle\sum_0\{A(x_0^2+y_0^2-2z_0^2)+B(x_0^4+y_0^4-2z_0^4)\}/\sqrt{3}+\cdots, \end{aligned} \tag{12}$$

$$\begin{aligned} V_4&=\textstyle\sum_0\{Cx_0y_0+E(x_0^3y_0+x_0y_0^3)\}+\cdots, \\ V_5&=\textstyle\sum_0\{Cx_0z_0+E(x_0^3z_0+x_0z_0^3)\}+\cdots, \\ V_6&=\textstyle\sum_0\{Cy_0z_0+E(y_0^3z_0+y_0z_0^3)\}+\cdots, \end{aligned} \tag{13}$$

$$V_{19}=\textstyle\sum_0E(x_0y_0^3-x_0^3y_0), \quad V_{20}=\sum_0E(z_0x_0^3-z_0^3x_0), \quad V_{21}=\sum_0E(y_0z_0^3-y_0^3z_0) \tag{14}$$

where A, B, C and E are centro-symmetric, i.e., functions only of r_0. The simplest supposition to make is that the field from the corner atoms is similar to that from a point charge, whose magnitude e_{EFF} need not coincide with that of an electron, or else that this field is like that from a dipole μ which is always directed away from the central ion. It doubtless appears a better approximation to treat the water molecules as dipoles than as charges, but it must be mentioned that in our dipole approximation we do not attempt an accurate examination of the delicate question of just how much the dipole turns during the motion. Instead it is assumed that the dipole is radially directed throughout the entire vibration. Because of the anisotropic character of dipole fields, any other supposition would lead to excessive mathematical difficulties. The final results with the charge and dipole approximations do not differ too greatly, at least from a qualitative standpoint, and this fact shows that our conclusions are not very sensitive to the particular character of the model.

With $f_{0i}=-ee_{EFF}/r_{0i}$ it is found that

$$\begin{aligned} A&=\tfrac{1}{4}ee_{EFF}(18R^{-4}-75R^{-6}r_0^2), \quad B=175ee_{EFF}/8R^6, \\ C&=ee_{EFF}(-6R^{-4}+15R^{-6}r_0^2), \quad E=-35ee_{EFF}/2R^6, \end{aligned} \tag{15}$$

while for the dipole case $f_{0i}=e\mu/r_{0i}^2$

$$A=-\tfrac{1}{4}e\mu(72R^{-5}-450R^{-7}r_0^2), \quad B=-525e\mu/4R^7, \quad C=e\mu(24R^{-5}-90R^{-7}r_0^2), \quad E=105e\mu/R^7. \tag{16}$$

The expressions (15, 16) have been carried through terms of the fourth order in r_0. If we can neglect the overlapping of the Y atoms by the d electrons, this termination with r^4 is rigorous, because of the orthogonality of ψ^2 to high order terms in the development, as explained more thoroughly in note 4 of the preceding paper. We will later estimate e_{EFF} or μ from the cubic splittings found by Schlapp and Penney in various salts of the iron group. Since the waters surrounding a cation are negatively polarized, e_{EFF} will be negative, and μ positive.

Some remarks must be made concerning the terms in (7) which are quadratic in the Q's. Their coefficients, for which Greek letters are used, can for our purposes be regarded as independent of x_0, y_0, z_0, so that they do not involve any degeneracy difficulties, or depend on the orientation of the central atom's charge cloud. Actually, these coefficients may depend somewhat on the x_0, y_0, z_0, because the Jahn-Teller complications are linear in the coordinates only in the first approximation. The latter, however, is sufficient to lift the degeneracy, and consideration of higher order approximations would be superfluous in the present state of the theory. The various coordinates do not appear merely as squares without cross products, for the Q's (or Q''s) are normal coordinates only as long as there is cubic symmetry. Actually, the cluster XY_6 is embedded in a field of only trigonal symmetry, and so they partially lose their normal property, unless we are interested in the problem of free molecules rather than of solids. The factorization in the squared terms thus corresponds to the group C_{3i} rather than O_h. The behavior as regards the representations of the group C_{3i} is, in Mulliken's notation,[5] as follows:

$$A_g: Q_1;\ Q_4';\ Q_{19}'. \quad E_g: (Q_2, Q_3);\ (Q_5', Q_6');\ (Q_{20}', Q_{21}').$$

These results can either be verified directly, or taken from Mulliken's[5] tables for the reduction of representations of given symmetry into those of lower symmetry. A and E are respectively the single and twofold trigonal representations.

There will in general be cross terms between different normal coordinates belonging to the same representation when repeated. However, by choosing coordinates in such a manner that they transform in the same way, the cross terms of this particular type can be somewhat simplified as has been done in (7). For instance, for the cross terms connecting (Q_2, Q_3) with (Q_5', Q_6'), involve only the products Q_2Q_5' and Q_3Q_6', not Q_2Q_6' or Q_3Q_5'. The coefficients V_k not only belong to the same irreducible representation as the Q_k, but also must transform in the same way, and so have the same basis, rather than one differing by an equivalence transformation. The necessary consistency is, however, automatically achieved as long as the calculation is made explicitly, as in our computation.

The point of using Q_4', Q_5', Q_6' rather than Q_4, Q_5, Q_6 is that we have then separated the representation $A_g(Q_4')$ from $E_g(Q_5', Q_6')$. Similar advantages apply to use of Q_{19}', Q_{20}', Q_{21}' in place of Q_{19}, Q_{20}, Q_{21} as then $A_g(Q_{19}')$ is resolved from $E_g(Q_{20}', Q_{21}')$. This factorization is not secured with the unprimed variables. It is true that (Q_4, Q_5, Q_6) or (Q_{19}, Q_{20}, Q_{21}) transform irreducibly for the cubic group, which is adequate for consideration of the Jahn-Teller effect in a free molecule XY_6, but there is only trigonal symmetry when this cluster is embedded in the whole alum crystal. It is because of the latter complication that the purely rotational coordinates Q_{19}', Q_{20}', Q_{21}' appear in (7); in the crystal, rotation of the entire system XY_6 no longer leaves the potential energy invariant.

4. The Secular Determinant

Throughout, we suppose that the spacing between the different cubic families of states, i.e., between different characteristic values of V_{cubic}, to be so large that we may neglect all off-diagonal elements except those connecting states which coincide in a cubic field. Our secular problem is thus one internal to a given cubic representation Γ, and the secular equation is

$$\left|\left(\sum_{k=2}^{6} V_kQ_k + V_{\text{trig}}\right)(n';n) - \delta(n';n)(W-W_0)\right| = 0, \tag{17}$$

where n, n' specify the various substates of Γ. When the roots of (17) are found, they are to be so chosen as to minimize W, i.e.,

$$\partial W/\partial Q_k = 0 \qquad (k=1, \cdots, 6). \tag{18}$$

In connection with (17, 18) it is to be noted that the Q_k enter in (17) not only explicitly but also

through W_0, since by (7) the diagonal member W_0 contains a large number of quadratic terms in the Q's, as well as the linear term cQ_4'.

We may suppose that V_{trig} has the form

$$V_{\text{trig}}=\sum_0[(G+30Hr_0^2)(x_0y_0+y_0z_0+z_0x_0)-35H(x_0y_0^3+x_0^3y_0+x_0z_0^3+x_0^3z_0+x_0z_0^3+y_0z_0^3+y_0^3z_0)], \quad (19)$$

where G and H are independent of x_0, y_0, z_0. As explained in the previous paper,[6] this is the most general trigonal potential for our purposes, since we can surely neglect the overlapping of the charges of the central ion and the atoms outside the water group.

The construction of the matrix elements is most easily achieved by supposing that the orbital wave functions of the central atom are such that Russell-Saunders coupling is a good approximation, i.e., that the ll and ss coupling is large compared to the cubic field. One may then use the matrix elements of x_0^2, x_0y_0, etc. given by Penney, Schlapp and Jordahl.[7] Because (12–13) are of the fourth degree in the electronic coordinates, it would at first sight seem that one would have also to reckon out all the matrix elements of x_0^4, $x_0^3y_0$, etc., many of which have not been published. However, this is not really necessary. Instead it is only necessary in each determinant to compute one non-vanishing element involving $x_0^4-y_0^4$ (or, if preferred $x_0^4+y_0^4-2z_0^4$), and one involving $x_0^3y_0+x_0y_0^3$. The reason is the V_2, V_3 transform like an irreducible representation Γ_3 of the cubic group, while V_4, V_5, V_6 transform like Γ_5. Furthermore, our basis or wave functions transform like some irreducible representation of the cubic group. Under these conditions, group theory uniquely determines the matrix elements except for a proportionality factor, and in general except for an equivalence transformation, but the latter need not concern us, as our quadratic and biquadratic terms which appear together in expressions such as (12–13) transform similarly. Hence the ratios of the matrix elements can be determined by keeping only the quadratic terms, and the absolute value fixed by computing one element with the full expresson. In short, group theory uniquely fixes the structure of the various secular determinants given below, except that it does not fix the absolute values of the coefficients a, b, t, a' in later equations such as (21). For this reason, our assumption of Russell-Saunders coupling involves no essential loss of generality. Its breakdown by the cubic field would merely modify our definitions of a, b, t, etc.

Before use can be made of the usual matrix elements of X^2, X^4 etc., it is necessary to express our irreducible cubic basis functions in terms of wave functions ψ_{LM_L} appropriate to the ordinary L, M_L system of quantization. The appropriate formulas are[8]

$$\psi(P\Gamma_4)=\psi_{10},\ \psi_{11}^+,\ \psi_{11}^-; \qquad \psi(F\Gamma_4)=\psi_{30},\ -\sqrt{\tfrac{5}{8}}\psi_{33}^+ +\sqrt{\tfrac{3}{8}}\psi_{31}^+,\ \sqrt{\tfrac{5}{8}}\psi_{33}^- +\sqrt{\tfrac{3}{8}}\psi_{31}^-,$$

$$\psi(D\Gamma_5)=\psi_{22}^-,\ \psi_{21}^-,\ \psi_{21}^+; \qquad \psi(F\Gamma_5)=\psi_{32}^+,\ \sqrt{\tfrac{3}{8}}\psi_{33}^+ +\sqrt{\tfrac{5}{8}}\psi_{31}^+,\ \sqrt{\tfrac{3}{8}}\psi_{33}^- -\sqrt{\tfrac{5}{8}}\psi_{31}^-,$$

$$\psi(D\Gamma_3)=\psi_{20},\ \psi_{22}^+.$$

The superscripts $^{\pm}$ mean that a cosine or sine rather than exponential azimuthal factor is to be used with, of course, the understanding that in every case the ψ functions are normalized to unity. The P functions obviously furnish the easiest means of getting the structure of the secular determinant for Γ_4 or Γ_5,[9] but F or D states are involved in the magnetic applications, and their detailed wave functions are necessary to fix the absolute value of the matrix elements.

The secular equation has a different structure in case the cubic state is Γ_3 or Γ_4, Γ_5. The form turns out[9] to be the same for Γ_4 and Γ_5 and is as follows

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[6] For simplicity in printing, we omitted the summation over the d electrons in the corresponding Eq. (6) of the preceding paper.

[7] Penney and Schlapp, Phys. Rev. **41**, 194 (1932); Schlapp and Penney, *ibid.* **42**, 666 (1932); O. Jordahl, *ibid.* **45**, 87 (1934).

[8] See p. 166 of Bethe's paper, reference 5.

[9] The similarity in structure for the Γ_4 and Γ_5 determinants can not only be verified by explicit computation, but is also a necessary consequence of the fact that by (8) the same representations are contained in the corresponding symmetrical direct products.

$$0=\begin{vmatrix} W_0+2\sqrt{3}aQ_3-W & bQ_5+t & bQ_6+t \\ bQ_5+t & W_0-3aQ_2-\sqrt{3}aQ_3-W & bQ_4+t \\ bQ_6+t & bQ_4+t & W_0+3aQ_2-\sqrt{3}aQ_3-W \end{vmatrix}. \tag{21}$$

The values of a, b, and t depend on the representation and L value. If the corner atoms act like point charges, so that Eqs. (15) apply, then it is found after straightforward, though somewhat lengthy calculation that

$$P\Gamma_4 \quad a=-3\rho_1/5, \qquad b=-6\rho_1/5, \qquad t=-6\tau_1/5, \tag{22a}$$

$$F\Gamma_4 \quad a=-2\rho_1/5-25\rho_2/132, \quad b=\rho_1/5+5\rho_2/11, \quad t=\tau_1/5+5\tau_2/11, \tag{22b}$$

$$D\Gamma_5 \quad a=3\rho_1/7-25\rho_2/63, \quad b=-6\rho_1/7+10\rho_2/21, \quad t=-6\tau_1/7+10\tau_2/21, \tag{22c}$$

$$F\Gamma_5 \quad a=0+175\rho_2/396, \quad b=\rho_1+5\rho_2/33, \quad t=\tau_1+5\tau_2/33 \tag{22d}$$

with $$\rho_1=ee_{EFF}C_1\overline{r_0^2}/R^4, \quad \rho_2=ee_{EFF}C_2\overline{r_0^4}/R^6, \quad \tau_1=-C_1G\overline{r_0^2}/6, \quad \tau_2=2C_2H\overline{r_0^4}. \tag{23a}$$

If the dipole rather than charge model is used, the definitions of ρ_1, ρ_2 become

$$\rho_1=-4e\mu C_1\overline{r_0^2}/R^5, \qquad \rho_2=-6e\mu C_2\overline{r_0^4}/R^7. \tag{23b}$$

Here the bars over r^2, r^4 denote respectively the mean square and mean fourth power radius of the electron. The factors C_1 and C_2 are inserted to allow for the fact that the matrix elements of a system of several electrons in Russell-Saunders coupling in general differ by a proportionality constant from those of a one-electron system having the same L value. For instance, they are not the same for f^2F and $d^2\,{}^3F$. The conversion factor has different values C_1, C_2 for the second and fourth degree terms, but is the same for all the terms of given degree that we encounter. With only one electron, C_1 and C_2 of course equal unity. With more than one electron and our Coulomb model, the values of C_1 and C_2 may be calculated from the invariance of the diagonal sum,[10] and are as follows

$$C_1(d^2\,{}^3F)=-C_1(d^2\,{}^4F)=3/7, \quad C_2(d^2\,{}^3F)=-C_2(d^2\,{}^3F)=-11/7. \tag{24}$$

If sometimes convenient to throw (21) into a form in which Q_4' rather than Q_2, Q_3 appears only on the principal diagonal. This change is particularly convenient in case the most important type of Jahn-Teller effect is trigonal rather than tetragonal, or in case it is of interest to diagonalize the natural trigonal field. The secular equation (21) then becomes (with printing of $W-W_0$ omitted)

$$0=\begin{vmatrix} \frac{2}{3}\sqrt{3}bQ_4'+2t & \sqrt{6}aQ_3+\frac{1}{3}\sqrt{3}bQ_6' & -\sqrt{6}aQ_2+\frac{1}{3}\sqrt{3}bQ_5' \\ \sqrt{6}aQ_3+\frac{1}{3}\sqrt{3}bQ_6' & \sqrt{3}aQ_3-\frac{1}{3}\sqrt{3}bQ_4'-\sqrt{\frac{2}{3}}bQ_6'-t & \sqrt{3}aQ_2+\sqrt{\frac{2}{3}}bQ_5' \\ -\sqrt{6}aQ_2+\frac{1}{3}\sqrt{3}bQ_5' & \sqrt{3}aQ_2+\sqrt{\frac{2}{3}}bQ_5' & -\sqrt{3}aQ_3+\sqrt{\frac{2}{3}}bQ_6'-\frac{1}{3}\sqrt{3}bQ_4'-t \end{vmatrix}. \tag{25}$$

The corresponding equivalence transformation is

$$\psi=(\psi_1+\psi_2+\psi_3)/\sqrt{3}, \quad \sqrt{\tfrac{2}{3}}[\psi_1-\tfrac{1}{2}(\psi_2+\psi_3)], \quad [\psi_2-\psi_3]/\sqrt{2}, \tag{26}$$

where ψ_1, ψ_2, ψ_3 is the basis of (21).

The secular determinant for Γ_3 is considerably simpler than for Γ_4 or Γ_5. Its form is

Γ_3

$$0=\begin{vmatrix} -a'Q_3+W_0-W & a'Q_2 \\ a'Q_2 & a'Q_3+W_0-W \end{vmatrix} \tag{27}$$

with $$a'=[(6\rho_1/7)+(25\rho_2/42)]\sqrt{3}.$$

[10] See Penney and Schlapp, Phys. Rev. **41**, 201; J. H. Van Vleck, *ibid.* **41**, 211 (1932).

It will be noted that there are no terms in Q_4, Q_5, Q_6, as we already predicted from group theory. Also V_{trig}, which behaves like Q_4', does not enter.

5. Minimization of the Roots of the Secular Determinant

We now seek to determine the values of the Q's which will make the roots of our secular equation satisfy the minimum or equilibrium conditions (18). In the case of Γ_3, this equation is only a quadratic, and there is no particular algebraic difficulty. When use is made of (7), a set of simultaneous equations is obtained which determine $Q_2^2+Q_3^2$, and the ratios $Q_5'/Q_2=Q_6'/Q_3$ and $Q_{20}'/Q_2=Q_{21}'/Q_3$. However, the ratio Q_3/Q_2 is indeterminate, so that there are an infinite number of possible displacements which will yield the same energy. If one neglects the coupling due to the natural trigonal field, the coefficients κ and λ in (7) vanish, and $(Q_2^2+Q_3^2)^{\frac{1}{2}}=a'/\beta$. The shift in energy as compared with that for zero values of the Q's is $\Delta W=-(a')^2/2\beta$. The situation is quite different than that for Γ_4, Γ_5, as we will soon see that with Γ_4, Γ_5 there are only a finite number of equivalent displacements of equal energy. With Γ_3, however, the locus of minimum energy is a circle in the Q_2, Q_3 plane, and the system will describe this circle when vibrational energy is considered. The case where Γ_3 is the lowest state does not appear to be one of particular practical importance. It would be realized if there were a copper alum, or a complex salt of equivalent crystal structure. Even then, the Jahn-Teller effect would be less significant than usual, as the representation Γ_3, though degenerate, by exception carries no orbital magnetic moment, and so there are not the usual repercussions of degeneracy on the magnetic susceptibility. We therefore pass on to the more vital cases Γ_4, Γ_5.

Unfortunately, the secular equations for Γ_4, Γ_5 are cubics, and so an explicit solution in the general case is not feasible. However, it is possible to pick out certain solutions which possess unusual symmetry properties, and which often satisfy the requirement of having lower energy than adjacent roots corresponding to slightly different values of the Q's. They thus represent true minima with respect to small variations of Q, but it does not follow that they are the lowest minima. Without any great error we can assume that the coefficients θ, κ, ω, ν in (7) which couple Γ_5 with other cubic representations Γ_1, Γ_4 are zero, as they would vanish for a free XY_6 molecule, and exist only in virtue of the noncubic portion of the outside field due to the rest of the crystal, i.e., what we may call the natural trigonal field. We will henceforth neglect these coefficients in the interest of mathematical simplicity. Then there exists a very simple solution in which Q_4' alone is excited, and the other Q's are zero; *viz.*,

$$Q_4'=(-\tfrac{2}{3}\sqrt{3}b-c)/\gamma, \quad \Delta W=2t-2(+\tfrac{1}{3}\sqrt{3}b+\tfrac{1}{2}c)^2/\gamma. \tag{28}$$

Here ΔW denotes the displacement in energy as compared with that which obtains when the Q's are zero, and when further there is no natural trigonal field (i.e., $t=0$). There are also three solutions very closely related to (28) and which differ for a free XY_6 molecule only in that they involve distortion along one of the three other body diagonals of the octohedron rather than that $x=y=z$ which serves as the trigonal axis in (28). Mathematically, these solutions are constructed by reversing the signs of two of the three quantities Q_4, Q_5, Q_6 in the definition (5) of Q_4'. Correspondingly the signs of two of the three ψ_i in (26) are reversed. The terms involving c, t will not have the same value as in (28), since the three other body diagonals are not the same as the natural trigonal axis. It can be shown that as long as the natural trigonal field is small compared with the Jahn-Teller effect, then for these other solutions

$$\Delta W=-\tfrac{2}{3}t-2(\tfrac{1}{3}\sqrt{3}b-\tfrac{1}{6}c)^2/\gamma-4t^2\gamma/9b^2. \tag{29}$$

Another type of solution is that in which the coordinates Q_2 and Q_3 are excited and in which Q_4, Q_5, Q_6 are zero. The corresponding distortion is essentially tetragonal rather than trigonal. If we neglect all coefficients, including c, t, which exist only in virtue of the natural trigonal field,

and which complicate matters by coupling together the tetragonal and trigonal modes of vibration, then, we find that

$$Q_2=0,\quad Q_3=-2\sqrt{3}a/\beta \quad \text{or else} \quad Q_2=\pm 3a/\beta,\quad Q_3=-\sqrt{3}a/\beta;\quad \Delta W=-6a^2/\beta. \tag{30}$$

The different choices represent the equivalence of the three possible tetragonal axes. In all three cases the value of ΔW is the same.

It can be proved that as long as the influence of the natural trigonal field is entirely neglected ($c=t=0$), our solution (28), and its three equivalent solutions (29) differing merely in the selection of a body diagonal gives the least energy of all distortions of the trigonal type Q_4', Q_5', $Q_6'\neq 0$, $Q_2=Q_3=0$, and that (30) has a corresponding minimum property for the tetragonal variety Q_2, $Q_3\neq 0$, Q_4', Q_5', $Q_6'=0$. What we have not been able to prove is that there is not some linear combination of the tetragonal and trigonal types of distortion which gives lower energy than either alone. In fact, the coefficient κ due to the natural trigonal field couples together Q_2, Q_3 and Q_5', Q_6', so that strictly speaking, only Q_4' can be excited alone. However, if the trigonal coefficient b is large compared with the tetragonal, the deepest energy presumably corresponds to nearly trigonal distortion and vice versa. Namely, it can be shown[11] that if $b^2>6a^2\gamma/\beta$ and if we neglect κ, ν, t, c then the solutions (28), (29) are stable as compared with those in which small amounts of Q_2, Q_3 are superposed, and that the purely tetragonal solutions (30) are stable if $a^2>b^2\beta/9\gamma$.

In the preceding minimization of the solutions of the secular determinant we have treated the natural or c, t terms as less important than the others. If the reverse is true, our procedure requires some modification. One root of the secular determinant is then given by (28) and the other two roots W', W'' can be obtained from a quadratic secular determinant constructed from the lower right rows and columns of (25), as the matrix elements connecting different eigenvalues of V_{trig} can now be neglected. So

$$W',\ W''=W_0-\tfrac{1}{3}\sqrt{3}bQ_4'-t\pm[3a^2(Q_2^2+Q_3^2)-4ab(Q_2Q_5'+Q_3Q_6')+\tfrac{2}{3}b^2(Q_5'^2+Q_6'^2)]^{\frac{1}{2}}. \tag{31}$$

The application of (18) to (31) determines Q_2/Q_5' and Q_3/Q_6' but not Q_2/Q_3. The situation is thus similar to the case of Γ_3 discussed at the beginning of the section, as there are now an infinite number of displacements of equivalent energy. Whether (28) or (31) represents the lower energy depends on the sign of t.

6. Numerical Estimates

We must now seek to estimate the numerical magnitude of the shifts in energy due to the Jahn-Teller effect which we have computed in the preceding section, and examine whether they are large enough to influence the magnetic susceptibility. To do this, we must first of all evaluate a, b. Six changes or dipoles, octohedrally arranged, give rise to a fourth-order cubic potential

$$\sum_0 D'[x_0^4+y_0^4+z_0^4-(3r_0^4/5)] \quad \text{with} \quad D'=-35ee_{EFF}/4R^5 \quad \text{or} \quad D'=175e\mu/4R^6. \tag{32}$$

By means of (32), e_{EFF} or μ can be determined if we use the empirical value of the fourth-order coefficient D' deduced by Schlapp and Penney[12] from the analysis of magnetic susceptibilities. The quantity Dq in terms of which they express their results is not quite the same as our D', but is connected with the latter as follows

$$Dq=D'\overline{r^4}(2/105). \tag{33}$$

According to them, Dq has the value 1485 cm^{-1} for $Ni(SO_4)7H_2O$. Extensive measurements by

[11] This result is obtained by requiring that the total coefficient of Q_2^2 or Q_3^2 be positive. Part of this coefficient is that $\frac{1}{2}\beta$ contributed by (7); the rest comes from applying second-order perturbation theory to (25), so that the off-diagonal elements occur quadratically.

[12] Schlapp and Penney, reference 7, taking into account footnote 9 of Jordahl's paper, reference 7.

Krishnan and Mookherji[13] on a wide variety of hydrated nickel salts yield values of Dq ranging from 1096 to 1356 cm^{-1}. The comparatively small dependence on the material shows that the forces responsible for Dq come mainly from the six waters of coordination, and so it is not important that Dq be determined from an alum. It is probably even less important which paramagnetic ion (V^{+++}, Cr^{+++}, Ni^{++}, Cu^{++}) is involved, since the size of the cation and so the crystal structure is but little affected by the addition of d electrons. The analysis by Jordahl[7] of the susceptibilities of certain cupric salts gives $Dq=1890$ cm^{-1}. The experimental measurements by Janes[14] on the Curie constant of $K_3Cr(SCN)_6\cdot 4H_2O$ yield values of Dq ranging from 1480 to 1720 cm^{-1}, but these estimates are very sensitive to the calibration of the absolute susceptibility. All the different evaluations of Dq agree in order of magnitude, and we may, probably to a sufficient approximation for our purposes, take $Dq=1500$ cm^{-1}.

For R we take the value 2.0A revealed by Lipson and Beevers'[4] x-ray work on the alums. To evaluate the mean square and fourth power radii needed in connection with (33) and (22), we use three-quantum hydrogenic wave functions, with the effective charge Z determined from the empirical ionization potential of Ti^{+++}, 43 volts. Then $Z=5.35$ and

$$\overline{r^2}=126a_0^2Z^{-2}=4.40a_0^2, \quad \overline{r^4}=25{,}515a_0^4/Z^4=31.2a_0^4, \quad (a_0=he/4\pi mc). \tag{34}$$

The alterations are inconsequential if instead we use an effective charge based on the ionization potential of V^{+++}, 48 volts. We thus find that

$$e_{EFF}=-1.01e \quad \text{or} \quad \mu=1.92\times 10^{-18} \text{ e.s.u.} \tag{35}$$

These estimates are of a reasonable order of magnitude. In fact, that of μ is quite close to the actual dipole moment 1.86×10^{-18} of the water molecule as revealed by dielectric constant data.[15] Such very good agreement is, however, probably accidental, as an accurate calculation of the fields from water molecules would have to allow for the finite length of the dipole, etc. The calculations of Z, of the mean values of r^2, r^4 and hence of e_{EFF}, μ are sensitive to the type of wave function assumed for the central atom. Nevertheless, the resulting uncertainty in our calculations is not as great as would seem, since by (23), (32) and (33), the expression Dq involves e_{EFF} or μ and r^4 in precisely the same fashion as do the fourth-order terms ρ_2 in (22), so that any uncertainties cancel out completely in the fourth-order part of (22), and all that is needed is the empirical value of Dq. The mean radii and effective charge or dipole moment are still needed in computing the ratio ($\sim\rho_1/\rho_2$) of the second- to the fourth-order portion of a, b, t in (22).

There is some reason for believing that we have slightly underestimated the effective charge in taking $Z=5.35$. This value of Z is based on the ionization potential required to remove one electron from our triply charged ion. Our justification for this procedure is that the outer part of the orbit is weighted heavily in the mean value of r^2 or r^4, and in this part the wave function becomes essentially that of a one-electron system, except for a different energy constant. Actually, as the orbits are nearly circular, in their classical analog, the contributions from the inner portions of the path are not negligible, and for the inner regions, the ionization potential to be used in determining Z is not that to remove one electron, but rather the mean potential, per electron, required to remove all the d electrons from the ion (i.e., one electron for Ti^{+++}, two for V^{+++}, and three for Cr^{+++}). If Z is determined in this fashion, it is augmented about 8 percent for V, and perhaps 20 percent for Cr, whose higher ionization potentials are unknown. This modification doubtless represents only an extreme limiting case, but even with it, the increases in Z are not serious. Probably a more real correction tending to raise Z is that the coefficient of the exponential in the wave function is not a simple power r^n, but rather a series of descending powers beginning with r^{n*}, so that this function projects out a little less to large values of r than we have supposed. On the other hand, any overlapping of the charge of neighboring atoms will tend to diminish Z

[13] Krishnan and Mookherji, Phil. Trans. Roy. Soc. **237**, 135 (1938).

[14] R. B. Janes, Phys. Rev. **48**, 78 (1935). Except for Jane's work, the determinations of Dq are all for divalent salts rather than the trivalent variety, such as we are concerned with. However, the addition of a d electron probably does not change greatly the size of the cation, and hence the distance to the waters of coordination responsible for the crystalline field.

[15] R. Sanger, Physik. Zeits. **31**, 806 (1930).

TABLE I. *Splittings $\Delta\nu$ and displacements for distortions of tetragonal type Q_2, Q_3.*

	CHARGE MODEL			DIPOLE MODEL		
	Q_3	$\Delta\nu$	$\Delta\nu/Q_3$	Q_3	$\Delta\nu$	$\Delta\nu/Q_3$
$^2D\Gamma_5$ (Ti^{+++})	1.51×10^{-9} cm	1650 cm^{-1}	1.10×10^{12}	0.66×10^{-9} cm	315 cm^{-1}	0.48×10^{12}
$^3F\Gamma_4$ (V^{+++})	0.14	15	0.11	0.83	495	0.60
$^4F\Gamma_5$ (excited Cr^{+++})	2.25	3660	1.63	2.70	5300	1.96

Fortunately any alterations in Z would have to be quite large to have an important bearing on the results. To get an idea what changes in Z do to the calculations, we may note that if Z is increased from 5.35 to $5.35\times(5/3)^{\frac{1}{4}}=6.95$ the results with the dipole model are the same as those for the charge model with Z kept at 5.35. This statement applies not only to the Jahn-Teller effect, but also to the indirect effect of the distant atoms discussed in the preceding paper, and is a consequence of the fact that substitution of the charge for dipole model increases the relative importance of the second- to fourth-order terms by a factor 5/3, while $r^2/r^4\sim Z^2$ (cf. Eqs. (32) and (34)). Comparison of the results which we will quote with the charge and dipole schemes shows that the difference between the two is not large enough to change the qualitative trend of the conclusions. Any increase in Z makes the direct effect of the distant atoms discussed in the preceding paper even less important than the estimates given there.

An objection which may be raised against our whole method of calculation is that we have included only the Coulomb fields connecting the d electrons with the water molecules, and have omitted the exchange forces which constitute the familiar repulsive mechanism in grating structures. However, the similarity of the alum crystal patterns and dimensions with various types of cations (Al, Ti, V, Cr, Fe) apparently indicates that the addition of d electrons has little effect, as long as the charge on the cation is kept the same, and that the repulsive forces are associated more with the s and p than the d shells. If so, these forces are irrelevant for our purposes. Any way, only their directional dependence, which may be rather small, enters in connection with the trigonal modes of distortion Q_4', Q_5', Q_6'.

The restitution coefficients β, γ needed in Eq. (28), etc. are connected with the frequencies ν_2, ν_3 for the modes shown in Fig. 1 by the relations

$$\beta=4\pi^2\nu_1^2M, \quad \gamma=4\pi^2\nu_2^2M, \tag{35}$$

where M is the mass of a corner atom, for our purposes a water molecule. We may provisionally take

$$\nu_2=\nu_3=300\ \text{cm}^{-1} \tag{36}$$

i.e.,

$$\beta=\gamma=5250\ \text{ergs/cm}^2. \tag{37}$$

This rough estimate is suggested by the values of the corresponding experimental Raman frequencies in molecules of the type XF_6, *viz.*[3]

$$SF_6,\ SeF_6,\ TeF_6: \quad \nu_2=642,\ 662,\ 672, \quad \nu_3=522,\ 402,\ 316\ \text{cm}^{-1}. \tag{38}$$

None of the examples (38) involves incomplete d electrons, and furthermore they all relate to free groups rather than those embedded in crystals. So none of them resembles our iron group too closely, and only qualitative information can be extracted from (38). The case of TeF_6 perhaps is nearest, as it involves an inter-atomic distance 1.84A greater than for the other cases (1.58, 1.70) and more nearly comparable with our value 2.00 of R. We adopt in (37) a somewhat lower value of ν than (38) because our water molecules are probably less firmly held to the central ion than are the fluorine atoms in (38), since water of hydration presumably represents less firm binding than a true chemical bond. The large shift in certain electronic absorption bands of chrome alum when deuterium is substituted for hydrogen[16] suggests that only the hydrogen out of the water participates in certain modes of vibration involving the paramagnetic ion. The frequencies of such vibrations would be very much greater than 300 cm^{-1}, but this change would not alter our rough estimates (37) of the restitution coefficients β, γ as the latter depend on potential energy rather than mass.

If we neglect the natural trigonal field, then the Jahn-Teller effects calculated from (28), (30), with constants determined according to (34), (35), (37), are given in Tables I and II for the various cases.

[16] H. Bohm, Ann. d. Physik **32**, 521 (1938).

TABLE II. *Splittings $\Delta\nu$ and displacements for distortions of trigonal type Q_4', Q_5', Q_6'.*

	CHARGE MODEL			DIPOLE MODEL		
	Q'_4	$\Delta\nu$	$\Delta\nu/Q_3$	Q_3	$\Delta\nu$	$\Delta\nu/Q_3$
$^2D\Gamma_5$ (Ti^{+++})	1.36×10^{-9} cm	1320 cm^{-1}	0.98×10^{12}	0.88×10^{-9} cm	550 cm^{-1}	0.63×10^{12}
$^3F\Gamma_4$ (V^{+++})	0.58	245	0.42	0.78	435	0.56
$^4F\Gamma_5$ (excited Cr^{+++})	0.68	330	0.49	0.44	135	0.33

In recording the values of the Q's we assume in Tables I and II that only the coordinates Q_3 and Q_4', respectively, are displaced, while the other Q's are zero. As explained in connection with Eqs. (28) and (30), there are two other equivalent tetragonal distortions, and three trigonal, in which other combinations of Q's in the group are excited, but in which the total displacement in the positions of the waters, and the splitting $\Delta\nu$ and energy shift ΔW are the same. We give in the tables not the values of the displacement ΔW in energy as compared with the unperturbed octohedral configuration, but rather the Stark splittings $\Delta\nu = -3W/h$ appropriate to the final perturbed or equilibrium values of the Q's. As explained at the end of Section III of the preceding paper, it is this splitting which acts as the centroid or important separation in the calculation of susceptibilities. The absolute magnitude of $\Delta\nu$ is three times[17] that of $\Delta W/h$. Because the Stark splittings are linear in the Q's, our estimates of them are still applicable, on the time average, even when allowance is made for the atomic or molecular vibrations. This fact is fortunate, as the amplitude associated with the zero point energy corresponding to (37) is 0.8×10^{-9} cm and so comparable with most of the J-T displacements.

In the last columns of the tables we give the ratio of the splittings to the coordinate displacement causing the separation. These ratios are applicable regardless of whether the displacement is automatically caused by the Jahn-Teller mechanism or arises from the indirect influence of distant atoms, which polarizes the water cluster, and is represented by the c term in (7). They furnish the basis of the numerical estimates of this indirect effect cited in the preceding paper.

The bearing of the results on paramagnetic relaxation will be discussed later. The application to magnetic susceptibilities is given in the preceding article. We there tacitly assumed that the tetragonal type of Jahn-Teller displacement does not give such low energy that the system prefers a tetragonal to a trigonal configuration. This supposition is seen to be warranted. The case of $F\Gamma_5$ constitutes an exception, but fortunately the J-T effect in this state is irrelevant for our purposes.[18] Reference to the tables shows that in V and Ti the energy displacements are apparently, under certain assumptions slightly larger for the tetragonal than the trigonal case, but the trigonal distortion will be stabilized, when allowance is made for the indirect effect of distant atoms. It is also stabilized when correction is made for the fact that ν_3 is probably lower than ν_2 (cf. Eq. (38)), rather than equal as assumed in (37), so that (28) will have a smaller denominator than (30).

[17] The factor 3 arises for the following reasons. The displacement in Stark (i.e., charge or dipole) energy is twice that in the total energy since at the equilibrium position (18) the Stark displacement, which is linear in Q, is half-counterbalanced by an increase in the vibrational potential energy $\frac{1}{2}\beta Q_3^2$ or $\frac{1}{2}\gamma(Q_4')^2$ as compared with the unperturbed value zero. Clearly at the minimum of an expression of the form $aQ+bQ^2$, the term aQ is twice as large as bQ^2. This effect gives a factor 2 since the Stark energies contribute to the splittings, whereas ordinary vibrational potentials do not. There is an additional factor $\frac{3}{2}$ because the separation between the appropriate roots of (21) or (25) is twice as large as the lowest root measured relative to the unperturbed value W_0.

[18] Cf. note 29 of the preceding paper.

On the Nature of the Solutions of Metallic Sodium in Liquid Ammonia*

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THE recent conclusion of F. Krüger[1] that solutions of sodium in liquid ammonia are colloidal and that therefore the interpretations of the magnetic measurements[2] require revision appears to us as untenable. That the solutions which Krüger prepared were colloidal, for a time, there can be little doubt. One would scarcely expect them to have been other than turbid from the manner he used to prepare them. Dropping a piece of sodium with a pair of pincers into a vessel and pouring in liquid ammonia must certainly lead to the formation of insoluble sodium hydroxide because of the moisture in the atmosphere. Sodium hydroxide admittedly acts as a catalyst for the decomposition of ammonia and the insoluble sodium amide results. The presence of these insoluble substances in fine suspension can account for Krüger's observations in the ultramicroscope.[3] However, it would appear unnecessary to speculate at length on what happens when metals are dissolved in liquid ammonia without those precautions which experimentation during the last fifty years has found indispensable.[4]

While we need not appeal to the magnetic behavior of these solutions to dispose of the assumption that they are colloidal (the strong lowering of the vapor pressure produced by dissolving sodium seems sufficient evidence against that assumption), we shall take this occasion to discuss the nature of these solutions in the light of the magnetic data. At 0.47 N the atomic susceptibility of sodium is about equal to that of solid sodium. This fact is consistent with the assumption of a colloidal solution. However, it is also consistent with the model of a free electron gas obeying the Fermi-Dirac statistics. On dilution, the atomic susceptibility increases continuously until at 0.0021 N, it is about one hundred times as great as at 0.47 N, that is, about two-thirds of the magnitude to be expected if the sodium is dispersed into independent "atomic" or "electronic" magnets distributed according to classical statistics. A further dilution did not increase the susceptibility per gram atom given by the 0.0021 N solution. This two-third value seems to have theoretical significance because the diamagnetism of *free* electrons cancels one-third of the paramagnetic susceptibility as Landau[5] has shown, and there-

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[1] F. Krüger, Ann. d. Physik **33**, 265 (1938).

[2] S. Freed and H. C. Thode, Nature **134**, 774 (1934); see also E. Huster and E. Vogt, Physik. Zeits. **38**, 1004 (1937).

[3] The color of the colloid first observed may have been conditioned by the sodium absorbed, occluded, or dissolved by the solid sodium amide or hydroxide. It is well known that alkali metals dissolve in molten sodium hydroxide and that sodium halides in the crystalline state absorb sodium vapor. The change in color with time may have been caused by the coagulation into bigger particles and also by the reaction of the sodium in the particles with the solvent. The inability of the solution to pass through the ultra-membrane filter as blue may have been due to the reaction of the sodium with the filter during the long time required for passage.

[4] For example, the solutions employed for our magnetic measurements were made entirely in a vacuum line. The tube in which the solution was to take place was flamed in a high vacuum (from 10^{-5} to 10^{-6} mm Hg). In this tube was condensed liquid ammonia which had been rigorously dried and twice distilled from sodium. The ammonia was then evaporated and the tube was flamed again at the high vacuum. This contact of the tube with liquid ammonia was to displace moisture in the glass. Connected to the tube was a capillary which was likewise flamed, pumped, etc., and to this capillary was joined another vessel containing sodium. The sodium was melted in a high vacuum to fill part of the capillary and then forced through the capillary to remove the nonmetallic hydroxide, etc., a procedure which is astonishingly efficient in producing bright metallic sodium in a high vacuum. The sodium was sent through the capillary by permitting propane gas (previously dried with sodium) at a pressure of several centimeters mercury to enter the vessels in which the sodium was melted. The capillary was then sealed off and liquid ammonia which had been twice distilled from sodium was condensed on the clean sodium. The solution was stirred with a glass tube in which a small iron rod had been sealed to permit movement by a magnet on the outside.

The solutions thus prepared scarcely changed their composition in metallic sodium in a week. Krüger's solutions seem to have greatly changed in several minutes. His most stable solution was decomposed (entirely ?) in about fifteen hours.

[5] L. Landau, Zeits. f. Physik **64**, 629 (1930).

fore the full freedom of the elementary magnets is actually accounted for. The independence of the elementary magnets (and incidentally the noncolloidal nature of the solutions) is confirmed further by the temperature coefficient of the susceptibilities. At the greater concentrations, the susceptibility drops with decreasing temperature but, at the greatest dilution we have measured, the susceptibility increases, its course appearing to conform roughly[6] with Curie's law and therefore to the independence of the elementary magnets in the classical sense.

To determine how closely the solutions approximate the idealization of a free electron gas Mr. Richard P. Metcalf in collaboration with one of us is re-investigating the solutions with apparatus of greater refinement. To him we are also indebted for suggestions in connection with this note.

[6] Perhaps because the deviation of the measurements from the mean is high in the temperature coefficients of these exceedingly dilute solutions.

Addendum

(December 16, 1938)

Our library has just received (December 13) a number of the *Annalen der Physik*[7] in which E. Huster reports the data which formed the basis of a previous paper by E. Huster and E. Vogt.[8] This we have referred to in the preceding note.

E. Huster also rejects the supposition of F. Krüger concerning the colloidal nature of the solutions which were measured magnetically. As remarked by E. Huster and E. Vogt, their data confirm in a general way the measurements of S. Freed and H. G. Thode but their data on the very dilute solutions are so scattered as to be inconclusive.

We shall refrain comment on these until more accurate data are available from this laboratory.

[7] E. Huster, Ann. d. Physik **33**, 477 (1938).
[8] E. Huster and E. Vogt, Physik. Zeits. **38**, 1004 (1937).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse abd contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Structure of the O−H Bands in the Vapors of Halogen Substituted Alcohols

In the study of the infra-red absorption of organic substances containing hydroxyl groups it has been found that the O−H bands sometimes occur as multiplets even though only one such group is present per molecule. This has been observed both in the spectra of vapors[1] and of solutions[2, 3] though in the latter case less structure is resolvable in some instances. The phenomenon has been explained by saying that the hydroxyl hydrogen is not free to rotate around the C−O bond, but may be found in more than one position of potential minimum in which the O−H frequency may be somewhat different.[1, 4] Though this explanation appears plausible it has seemed desirable to investigate the matter further by a quantitative study of some relatively simple substances in the vapor phase. Consequently a series of halogen substituted alcohols has been investigated with interesting results.

As has been shown previously[1] the third harmonic band of the primary alcohols is a doublet with components at about 10,510 and 10,460 cm^{-1}, of which the former is considerably the stronger. In ethylene chlorohydrin and bromohydrin a new and strong component makes its appearance at 10,367 and 10,318 cm^{-1}, respectively. The primary alcohol doublet persists, but appears to be shifted slightly to higher frequencies, and the low frequency component has become the stronger. In trimethylene chlorohydrin (3-chloro-1-propanol) and in the analogous bromine compound the spectrum, surprisingly enough, appears to be identical with that of a primary alcohol. If any new band is present it is very weak.

In propylene chlorohydrin (1-chloro-2-propanol) in addition to the ordinary band of the secondary alcohol at about 10,460 cm^{-1} a new intense component appears at 10,326 cm^{-1}. In symmetrical glycerol dichlorohydrin (1,3-dichloro-2-propanol) two intense bands occur at 10,243 and 10,325 cm^{-1}, while the band characteristic of the ordinary secondary alcohols has either disappeared or has become too weak to detect.

Some studies have been made of the effect of temperature on the relative intensities of the components of some of the O−H bands. In normal propyl alcohol the temperature effect was smaller than the experimental error, from which we conclude that the molecular configurations corresponding to the two components of the doublet differ in energy by not more than 800 cal. In ethylene chlorohydrin as the temperature is raised the primary alcohol doublet greatly increases in intensity at the expense of the strong band at 10,367 cm^{-1}. We estimate that the configuration corresponding to this last band is approximately 2,000 cal. lower in energy than those responsible for the doublet.

In orthochlorophenol the weak component of the doublet greatly increases in intensity with rise in temperature, but the effect has been somewhat difficult to measure quantitatively owing to the great difference in intensity of the two bands. Our results so far appear to indicate that there may be considerable differences in entropy between the different "tautomeric" configurations in which an alcohol may exist. Further details and more precise estimates of the heat effects will be given in a paper to follow.

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December 7, 1938.

[1] R. M. Badger and S. H. Bauer, J. Chem. Phys. **4**, 711 (1936).
[2] O. R. Wulf and U. Liddell, J. Am. Chem. Soc. **57**, 1464 (1935).
[3] P. Barchewitz and R. Freymann, Comptes rendus **204**, 1729 (1937).
[4] L. Pauling, J. Am. Chem. Soc. **58**, 94 (1936).

Infra-Red Absorption Spectrum of Benzoic Acid

Investigations of the infra-red absorption of benzoic and acetic acid dimers by Buswell, Rodebush and Roy[1] of this laboratory have shown two absorption peaks in the neighborhood of 3.5μ. Each of the peaks is a doublet, and it is believed that they are both due to hydrogen bond vibrations. This view is supported by the fact that both peaks disappear[1, 2] when deuterium is substituted for hydrogen in the acid position. It would therefore be expected that the deutero acids would likewise give two peaks, shifted of course, by reason of the mass effect.

However, the investigations of Buswell, Rodebush and Roy[1] for heavy benzoic acid did not extend quite far enough to show both peaks. They observed one absorption band at 4.46μ, which was near the limit of their observations. Calculations showed that the second band could be expected to appear at a wave-length slightly higher than the limit studied by them.

Accordingly a further investigation of the absorption of deutero benzoic acid was carried out in this laboratory with the result that a second band was observed at 4.83μ, in support of the theory. The absorption was studied for the acid in carbon tetrachloride solution under conditions

similar to those previously described.[1] The extended absorption curve for deutero benzoic acid together with other curves and a more complete theory of the vibrations of carboxylic acid dimers will be published shortly.

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November 21, 1938.

[1] A. M. Buswell, W. H. Rodebush and M. F. Roy, J. Am. Chem. Soc. **60**, 2239 (1938).
[2] R. C. Herman and R. Hofstadter, J. Chem. Phys. **6**, 534 (1938).

Molecular Association in Fatty Acids

In recent communications to this journal, Bonner, Hofstadter and Herman[1, 2] reported their work on the infra-red absorption spectra of heavy and light formic and acetic acids. Bonner and Hofstadter observe a definite shift of the O−H band in formic acid vapor from 3.25μ (3080 cm^{-1}) to 2.80μ (3570 cm^{-1}) as the vapor is raised from 25°C to 139°C. This they attribute to the formation of the monomer from the dimer at the higher temperature. Similar results are reported by Herman and Hofstadter[2] on heavy and light acetic acids. They find the bands 2299 cm^{-1} and 3125 cm^{-1} in the heavy and light acids sensitive to temperature, and at the higher temperature, these frequencies attributed to the deuterium and hydrogen bonds diminish in intensity while the free O−D and O−H bands appear at 2653 and 3640 cm^{-1}. These results point out to the existence of associated types of molecules in the fatty acids at laboratory temperature, which break up into lower polymers at higher temperatures.

By a study of the Raman spectra of formic, acetic and benzoic acids in different states, the author finds evidence similar to that presented by the above workers. The results of the author in acetic acid were published in a recent paper.[3] In all the three cases, it is found that the intensity maximum of the C=O band shifts to higher frequencies as the acid is diluted in water or heated up. In formic acid the C=O maximum shifts from 1702 cm^{-1} at 95 percent to 1728 at 48 percent concentration and the band gets flattened by heating the acid from 30° to 100°C. In acetic acid the C=O maximum shifts from 1673 at 100 percent to 1710 solution in water at 25 percent and from 1673 at 30°C to 1700 at 100°C and in benzoic acid from 1654 in the molten state to 1728 in a solution in water. Dilution in a nonpolar solvent like benzene or carbon tetrachloride does not produce this result. The C=O band is more or less unaffected. During processes of association, it is well known that it takes place by forming a hydrogen bond between the O of the C=O of one molecule and the H of OH of the other. Hence the C=O bond strength is reduced with the external attachment and its frequency diminishes. The shifting of the C=O frequencies to higher values at higher dilutions and at higher temperatures indicates the predominence of the lower polymers having higher frequencies at these dilutions and temperatures. The depolymerization effected by dilution in water is in good accord with physico-chemical evidence which points to such a dissociation when a polar substance is dissolved in a polar solvent. Dissociation does not take place when a polar and a nonpolar substance are mixed which explains the fact that no change is observed in the C=O band of the three acids studied when they are dissolved in benzene or carbon tetrachloride.

These results are also in accord with the previous results obtained in water and heavy water by Ramakrishna Rao[4] Cross, Burnham, Leighton[5] and the author,[6] where it was observed that the components of higher frequency increased in intensity at higher temperatures. Ramakrishna Rao and the author attributed these changes to the breaking up of the associated water and heavy water molecules into simpler ones at the higher temperatures.

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October 27, 1938.

[1] L. G. Bonner and R. Hofstadter, J. Chem. Phys. **6**, 531 (1938).
[2] R. C. Herman and R. Hofstadter, J. Chem. Phys. **6**, 534 (1938).
[3] P. Koteswaram, Zeits. f. Physik **110**, 118 (1938).
[4] I. R. Rao, Proc. Roy. Soc. London **A92**, 496 (1931).
[5] P. C. Cross, J. Burnham and P. A. Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).
[6] P. Koteswaram, Ind. J. Phys. **12**, 63 (1938).